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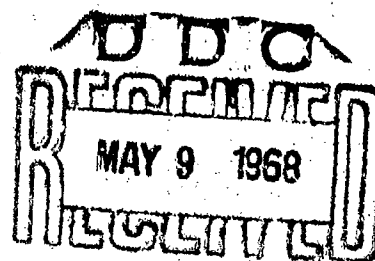
**CASTABLE HEAT RESISTANT EXPLOSIVE COMPOSITIONS
CAPABLE OF WITHSTANDING 500°F AND HIGHER**

(U)

by

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FOREWORD

Work was started in August 1963 to develop a castable explosive superior in heat resistance to the HMX/Laminac series and similar to or better than the compressible formulation, PBXC-8, based on DATB, Viton A, and Chemlock 607.

In the present study DATB and a number of more recently developed explosives were examined and compounded with various types of castable binders to observe compatibility, processability and stability characteristics. The most promising products were subjected to further investigation, including measurements of explosive properties and performance of theoretical calculations to predict the effect of additives and to optimize constituent ratios.

This report summarizes the findings of the first four years' investigation and presents recommendations for further study based on the preliminary results. The project was conducted under Task Assignments (1964) RUME TA-3E-015/216-1/F008-10-004 (Problem 15), (1965) RMMO-62-063/216-1/F009-08-05, (1966) ORD-033-201/200-1/F009-08-05 and is continuing in 1967 jointly under Navy Task Assignment ORD-033-201/200-1/F009-08-05 and Air Force MIPR PG 7-6. Additional reports will be issued routinely on a quarterly basis and additionally as warranted by the progress of the work.

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This report was reviewed for technical accuracy by Drs. C. D. Lind and M. H. Kaufman.

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NORMAN L. RUMPP, Head
Explosives and Pyrotechnics Div.
15 December 1967

Under authority of
G. W. LEONARD, Head,
Propulsion Development Dept.

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ACKNOWLEDGEMENTS

The assistance of the following in providing materials and suggestions, technical data and test results is gratefully acknowledged.

Jack Dierolf and Statistics Branch, computations and Ruby predictions.

Lily Koch, preparation and testing of compositions.

John Whitson and Richard Eppinger, evaluation of explosive properties.

Mary Pakulak and Otis Pennington, evaluation of physical and chemical properties.

Union Carbide Corporation and Dow-Corning Corporation, materials, suggestions and technical data.

Elsa Simmons, preparation of this report for publication.

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TATB	2,4,6-triamino-1,3,5-trinitrobenzene
TMD	theoretical maximum density
TNC	1,3,6,8-tetranitrocarbazole
Unox 207X	dicyclopentadienedioxide, Union Carbide
VDS	sym. divinyl tetramethyl disiloxane
Vi	vinyl
Vibrin	unsaturated polyesters, Naugatuck Chemical
VIPS	vinyl triisopropoxysilane
Viton A	copolymer of vinylidene fluoride and perfluoropropene, du Pont
VTs	vacuum thermal stability
Watson Standard 21-726	vinyl plastisol resin
XR-65	vinyl silicone resin, Union Carbide
Y3466/3467/KLI800	silicone system curing by silane condensation, Union Carbide
Z 6018	hydroxy functional cyclic siloxane intermediate, Dow-Corning
Z 6020	N- β -aminoethyl- γ -amino propyl trimethoxy silane, Dow Corning
Z 6030	methacryloxypropyl trimethoxysilane, Dow-Corning
Z 6077	1,3-bis(3-glycidoxy propyl)tetramethyl disiloxane, Dow-Corning

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INTRODUCTION

OBJECTIVES AND BACKGROUND

Increasing need for weapons and devices capable of withstanding severe environmental conditions encountered in modern military applications led to the initiation in August 1963 of a program to develop a castable explosive which could withstand temperatures of 500°F or higher. Compressible explosives are presently available which are resistant to temperatures in this general range. However, the most stable castable compositions in use today fall somewhat short of this goal, since they are based on HMX or on other explosive components of still lower heat resistance than that of HMX. Castable TNT formulations show relatively high decomposition points; however, these are limited in their use at higher temperatures because of the low melting point of TNT and the resultant problems arising due to exudation, dimensional instability, and segregation of components in the formulation.

Preliminary studies to formulate and characterize heat resistant compressible compositions were carried out at the Naval Weapons Center in 1958-1960. At this time the most promising explosive filler was diaminotrinitrobenzene (DATB). This material, when combined with fluorocarbon polymers as binders and pressed to desired size and shape, produced a composition with excellent physical properties and reasonably good stability when tested at temperatures of 300°F and 400°F over fairly prolonged periods of time. This work has been described in detail in a previous report (ref. 1).

More recently a number of new explosives have been synthesized which exhibit heat resistance superior to that of DATB. This characteristic as well as other possible advantages merit their investigation in both compressible and castable systems. Also much research effort has been expended during the past few years in a search for better binder materials for high temperature propellant and explosive applications. It would therefore be desirable both to re-examine the choice of possible components for a superior compressible composition as well as select the best candidates for castable applications. It is the purpose of this report to describe primarily efforts in the latter category as well as summarize information pertinent to both applications which might prove of value in upgrading compressible systems.

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METHOD OF APPROACH

Present castable explosive systems utilize either a melt-cast method of preparation or rely on polymerization of monomeric resins to achieve their final form. In the latter category both polyester and epoxy systems have been used to good advantage (refs. 2,3). The explosive filler is combined with liquid binder plus suitable curing agents, the mixture is then poured into warheads, and curing is accomplished either at ambient or elevated temperature as required to effect solidification. It was felt that this type of preparative procedure would be most advantageous in formulating high temperature compositions with presently available explosive fillers; therefore, initial efforts have been directed primarily toward finding suitable monomers and resins which are compatible with explosive fillers, can be cured readily to a desirable physical state, and possess thermal stability at least as good as that of the filler material.

In formulating a new castable explosive suitable for use in high temperature weapons systems a number of factors must be considered in addition to the heat resistance of the components. One of the most important is energy. Since most of the new high temperature filler candidates are considerably less energetic than either HMX or RDX, maximum solids loading is a prime requirement, especially if the castable binder itself is non-energetic. To achieve the highest possible filler content, the particle size distribution of the filler must be optimum and the binder viscosity and wetting properties must be favorable. Thus, possible crystal size and shape as well as solubility characteristics to permit ready recrystallization might have a bearing on final selection of an explosive candidate. In the case of a liquid, castable binder, low viscosity would be an essential factor.

In general the following steps were carried out in order to survey the best possibilities:

1. Information concerning possible filler material was compiled. This included data reported by other agencies, results of tests conducted at the Naval Weapons Center and estimates of future availability and cost.

2. Similar studies were made of suitable binder systems. Promising materials were evaluated in respect to their processability, qualitative physical characteristics, thermal stability, and compatibility with explosive fillers up to the decomposition point of the filler.

Methods for formulating and testing compositions are described in Appendices A and B.

3. A survey was made of heat resistant additives or co-fillers which might augment energy by improving density, oxygen balance, or solids

loading. Ruby calculations were carried out on a limited basis to optimize compositions and predict what magnitude of energy output might be possible with available working materials.

PRESENT STATUS

A number of candidate explosive fillers have been investigated, alone and in combination with a variety of binder formulations. The latter include polyesters, epoxies, phenolic types, PVC plastisols, some fluorocarbons, silanes, and siloxanes. Potential fillers include TACOT, a fairly recent duPont explosive, and the polynitrophenyl derivatives developed by the Naval Ordnance Laboratory during the past ten years. Compositions with autoignition points well above 300°C (572°F) are readily obtainable.

TACOT proved to be one of the best filler explosives in respect to heat resistance, with an autoignition point of over 350°C. TATB and HNS with ignition values of 325°C were also promising as far as thermal stability was concerned. However, these three explosives possess a number of disadvantages which render formulation of an acceptable composition very difficult. First, their energetic potential is quite low compared with that of HMX or RDX. In a castable system with an inert binder, it is doubtful that detonation velocities much greater than 6500-6800 meters per second could be achieved. At present their cost is high and their availability limited. TACOT and especially TATB are fine powders as synthesized, ranging from a mean of 30 microns down to less than 5 microns in particle diameter. Therefore, in order to obtain a desirable level of solids loading with a fluid binder, they should be recrystallized to obtain a more favorable size distribution. However, TATB is essentially insoluble in all common solvents, while TACOT is only slightly soluble in a few. The characteristics which impart high stability unfortunately tend to work in opposition to high energetic output and ease in processability.

HNS has not been studied as extensively as either TACOT or TATB because a suitable supply was not available in the earlier part of the program and its energy characteristics did not appear as favorable based on existing evidence. Its potentially lower cost and greater susceptibility to size modification make it a comparatively attractive candidate for future investigation. Other high temperature explosives such as DIPAM and NONA, while somewhat more feasible energywise, are not promising economically at present.

Evaluation of available binder types and formulations showed silicones to be the most heat resistant, with fluorocarbons next. Other polymers such as polyesters or epoxies did not possess the thermal stability of the silicones. Not only did the binders themselves fail to withstand comparable temperatures; in many cases binder reacted with explosive filler at temperatures considerably below the decomposition

point of the latter to produce violent exotherms which usually led to premature ignition.

The most promising formulation developed originally was one based on the explosive TACOT combined with a silicone RTV rubber diluted with a reactive vinyl or alkoxy silane to reduce the viscosity. This composition did not autoignite up to 350-360, the autoignition point of TACOT. Furthermore, the binder alone in oven tests showed comparatively good resistance at temperatures up to and exceeding the decomposition point of the filler. Although high loadability was not possible because of the small particle size of available filler, physical properties at the loadings obtained (50-60%) appeared attractive.

Further work with silicone polymers, however, has shown that this type of structure, the -O-Si-O backbone with pendant reactive groups, may act as an "energy sink" during detonation. Resulting velocities may range 200-400 meters per second lower than those observed when the same explosive filler is combined with a different polymer such as a polyester. Thus, in view of other difficulties with this type of system which detract from the total final output - loadability problems and low energy fillers - choice of a binder which would further augment these shortcomings would be somewhat inadvisable.

Until the "energy sink" effect was disclosed, the superior thermal resistance and commercial availability of silicone binders favored their acceptance over that of fluorocarbons. However, during the past few years more commercial interest has been displayed in the latter field and increased production should lower costs and improve selection of raw materials and intermediates. In general, vinyl fluorocarbon monomers are advantageous from the standpoint of viscosity and density. However, they are often difficult to cure, especially in the presence of fillers containing nitro groups.

EXPLOSIVE FILLERS FOR HIGH TEMPERATURE CASTABLE COMPOSITIONS

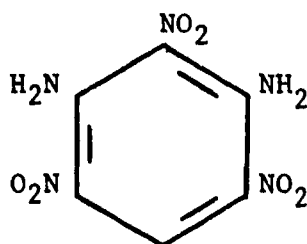
During the past ten years the Naval Ordnance Laboratory, White Oak, Maryland, has developed a number of heat resistant explosives based on benzene and polyphenyl derivatives (ref. 4). In addition, duPont has synthesized the explosive, TACOT. Some pertinent properties of these and several other explosives are compared in Table 1. More detailed information pertaining to those of particular interest is presented in the section following Table 1.

TABLE 1. Comparative Properties of Some Heat Resistant Explosives.

Explosives	Melting point, °C	Autoignition point, °C ^a	VTS, ml/g			Density, g/cc	Detonation velocity, m/sec
			260°C	280°C	Other		
DATB diaminotrinitrobenzene	275-280	295-305	3-4/hr ^b	52.5/hr ^b	Not significant/ 48 hr-100°C	1.83	7,600 - 98.2% TMD ^b
TATB triaminotrinitrobenzene	450 ^b	320-325	1.0-1.2/hr ^b	2.0/hr ^b	1.938 ^b	7,658 - 95% TMD ^b
TACOT tetranitrodibenzotetra- aza-pentalene	410 ^c	350-360	0.1/hr ^b	0.3/hr ^b	1.85	7,250 - 83% TMD ^c
HNS hexanitrostilbene	316 ^b	300-325	0.23-1.68/hr ^b	2.7/hr ^b	1.74 ^b	7,000 - 97.7% TMD ^b
NONA nonanitroterphenyl	440-450 ^b	375 ^{b, d}	0.5/hr ^b	0.89-3.7/hr ^b	1.78 ^b	7,400 - 95.5% TMD ^b
DIPAM diaminohexanitrobiphenyl	306 ^b	300 ^{b, d}	1.26-3.5/hr ^b	1.79 ^b	7,400 - 98.3% TMD ^b
TNC tetranitrocarbazole	293	310	0.07/51 hr/120°C	1.739 ^e	No experimental data.
PbN ₆ lead azide	>decomposition point	315 explodes	0.07/40 hr/100°C	4.80	5,180 - 83% TMD
Explosive "D" ammonium picrate	>decomposition point	265	0.4/40 hr/150°C	1.72	7,480 99+% TMD
Picric Acid trinitrophenol	122-123 ^f	295	0.5/40 hr/120°C	1.76	7,260 - 97% TMD
HMX cyclotetramethylene- tetranitramine	endothermic transition, 185g	255	0.6/48 hr/150°C	1.91	9,108 - 99+% TMD

^a 2°C temperature rise per minute. One gram samples. Referenced temperature is that of heating block.^b Data furnished by the Naval Ordnance Laboratory (NOL/WO), White Oak, Maryland.^c Data furnished by duPont.^d DIA.^e Data furnished by So. Dyestuffs Corporation.^f Reference 5.^g From autoignition thermogram.

DATB
2,6-diamino-1,3,5-trinitrobenzene



Autoignition Point, °C	295-305 (NWC)
Melting Point, °C	275-280 (NWC)
Impact Sensitivity	No fires, 300 cm (NWC) ^a
Friction Sensitivity	10/10 no fires, 440 kg-cm (NWC)
Electrostatic Sensitivity, 50% Pt.	4.65-8.03 joules (NWC)
Density, g/cm ³	1.83
Vacuum Thermal Stability	3-4 cc/g/hr @ 260°C (NOL) 52.5 cc/g/hr @ 280°C
Detonation Velocity, m/sec	7600 @ 98.2% TMD (NOL)
Heat of Formation, KC/mole	-29.23 (NOL)
Detonation Pressure, K-bar	251 @ 98.2% TMD (NOL)
Plate Push, ft/sec	3028 @ 93% TMD (NOL)
Size Range, μ	6-40 unless recrystallized
Solubility	Sol. DMF, DMSO
Cost per pound	\$7 - 50 depending on quantity
Suppliers	Holston, Northrup-Carolina

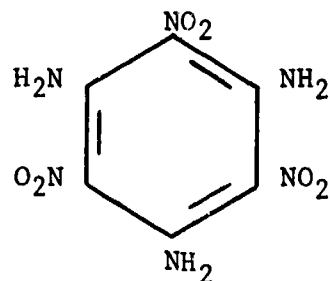
Advantages: Comparatively high energy, low cost, availability, ease in recrystallization, insensitiveness.

Disadvantages: Low melting point, inferior heat resistance.

References: Amcel correspondence, 1962-1965. (Refs. 6,7,8,9,10.)

^a Composition B = 36 cm

TATB
2,4,6-triamino-1,3,5-trinitrobenzene



Autoignition Point, °C	320-325 (NWC)
Melting Point, °C	450 (NOL)
Impact Sensitivity	no fires, 300 cm (NWC) ^a
Friction Sensitivity	10/10 no fires, 440 kg-cm (NWC)
Electrostatic Sensitivity, 50% Pt.	1.83 - 6.3 Joules (NWC)
Density, g/cm ³	1.938 (NOL)
Vacuum Thermal Stability	0.12-0.29 ml/g/48 hr, 120°C (NWC) 1.04-1.23 ml/g/hr, 260°C (NOL) 2 ml/g/hr, 280°C (NOL)
Detonation Velocity, m/sec	7658 @ 95% TMD (NOL)
Heat of Formation, KC/mole	-36.85 (NOL)
Detonation Pressure, K-bar	259 @ 95% TMD (NOL)
Plate Push, ft/sec	3124 ft/sec @ 93% TMD (NOL)
Size Range, μ	15-25 mean diameter (NWC)
Solubility	virtually insoluble in all common solvents
Cost per pound	\$150-200, 1-25 lb lots, 1965
Suppliers	Northrup-Carolina

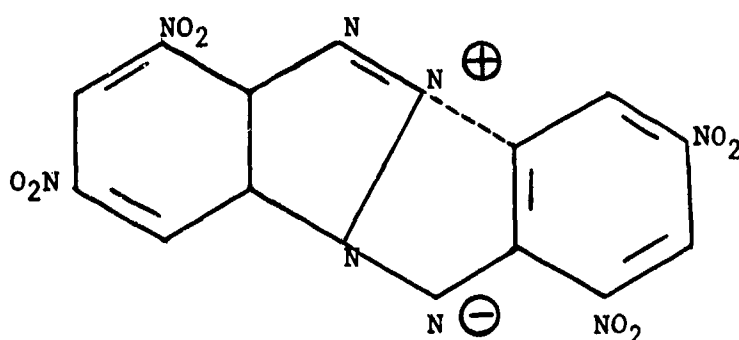
Advantages: Comparatively high energy, high density, low sensitivity, good heat stability.

Disadvantages: High cost, doubtful availability, fine size, insolubility.

References: 11 and 12.

^a Composition B = 36 cm

TACOT
Tetranitrodibenzo-1,3a,4,6a-tetraazapentalene



Autoignition Point, °C	350-360 (NWC)
Melting Point, °C	410 (du Pont)
Impact Sensitivity, 50% Pt. cm	66-89 (NWC) ^a 101 (NOL) ^b
Friction Sensitivity, 50% pt. kg-cm	418 to no fires at 440 (NWC)
Electrostatic Sensitivity, 50% Pt.	2.55 Joules (NWC)
Density, g/cm ³	1.85 (NOL)
Vacuum Thermal Stability	0.04-0.08 ml/g/48 hr, 120°C (NWC) 0.1 ml/g/hr, 260°C (NOL) 0.3 ml/g/hr, 280°C (NOL)
Detonation Velocity, m/sec	6448 @ 78.8% TMD (NOL) 7250 @ 89% TMD (du Pont)
Heat of Combustion, Cal/g	3545 (NOL)
Plate Push, ft/sec	2725 @ 93% TMD (NOL)
Explosive Power	96% TNT (du Pont)
Size Range, μ	20 median diameter (NWC)
Solubility	slight - nitrobenzene, DMF, DMSO, HNO ₃
Cost per pound	\$275, 2-10 lb lots
Suppliers	du Pont

Advantages: Excellent heat resistance, possibility of size modification.

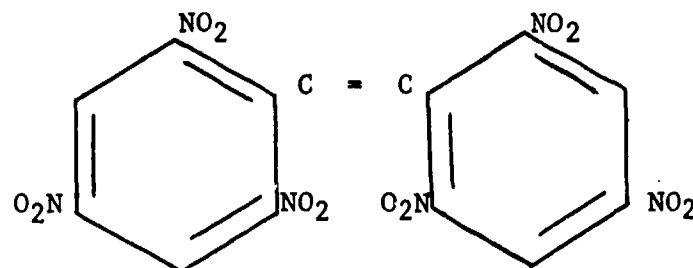
Disadvantages: Comparatively low energy, questionable availability.

References: du Pont correspondence, 1962. Ref. 13.

^a Composition B = 36 cm

^b Composition B = 60 cm

HNS
2,2',4,4',6,6'-hexanitrostilbene



Autoignition Point, °C	300-325 (NWC)
Melting Point, °C	313-318 (NOL)
Impact Sensitivity, 50% Pt, cm	39-61 (NOL)
	19-36 (NWC) ^a
Friction Sensitivity	10/10 no fires @ 440 kg-cm (NWC)
Electrostatic Sensitivity, 50% Pt.	3.6 Joules (NWC), 0.001 mfd, 8 KV, to 0.0001 mfd, 17 KV (NOL) ^b
Density, g/cm ³	1.74 (NOL)
Vacuum Thermal Stability	0.23-1.68 ^b cc/g/hr, 260°C (NOL)
	2.71-2.78 cc/g/hr, 280°C (NOL)
Detonation Velocity, m/sec	7000 @ 1.70 g/cm ³ (NOL)
Heat of Combustion, Cal/g	3451 (NOTS)
Size Range, μ	<10 - 725 (NOL) ^b
Weight Loss, 210°C, 48 hr	Negligible
Decomposition Rate at 500°F	0.1%/hr
Cost per pound	\$300 approx. ^c
Suppliers	Northrup-Carolina

Advantages: Potentially cheap, susceptible to size modification, thermally stable.

Disadvantages: Low energy, less heat resistant than TACOT, sensitive.

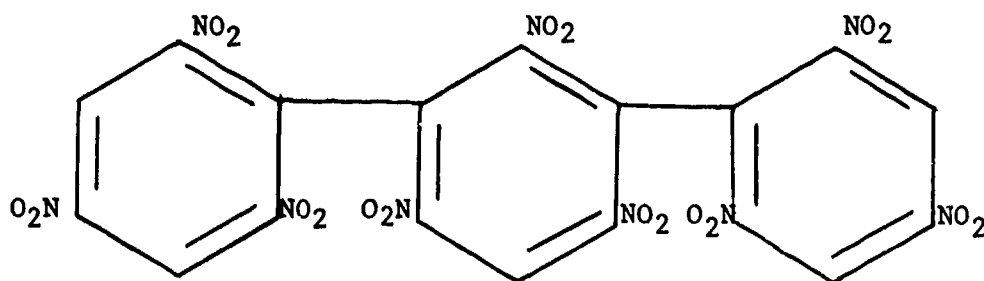
References: Ref. 4, 12, 14, 15, 16, 17.

^a Varies with grade. Difficult to measure because of light, fluffy consistency. NOTS: Composition B = 36 cm; NOL: Composition B = 60 cm.

^b May vary with grade.

^c Made from TNT and sodium hypochlorite. Price should come down with production.

NONA
2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl



Decomposition Point, °C, DTA	375 (Northrup-Carolina)
Melting Point, °C	440-450 (NOL)
Impact Sensitivity, 50% Pt	29-39 (NOL) ^a , 58 (Northrup-Carolina) ^b
Electrostatic Sensitivity	Fires >0.001 mfd @ 8 KV (NOL)
Density, g/cm ³	1.78 (NOL)
Vacuum Thermal Stability	0.5 cc/g/hr, 260°C (NOL)
	0.89-3.7 cc/g/hr, 280°C (NOL)
Detonation Velocity, m/sec	7400 @ 1.70 g/cm ³ (NOL)
Size Range, μ	10-150 μ (NOL)
Weight Loss, 210°C, 48 hr	0.5% (NOL)
Cost per pound	\$1,800 ^c
Suppliers	Northrup-Carolina

Advantages: Excellent thermal stability, fair energy.

Disadvantages: Costly and limited availability, somewhat sensitive.

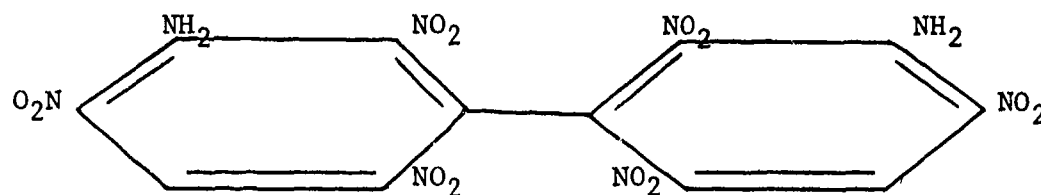
References: Ref. 3, 4, 15, 18, 19.

^a Composition B = 60 cm.

^b HMX = 65 cm.

^c Availability very limited. Made from dibromotrinitrobenzene and picryl chloride. Difficult to synthesize.

DIPAM
3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl



Decomposition Point, °C, DTA	300 (NOL)
Melting Point, °C	304-306°C (NOL)
Impact Sensitivity, 50% Pt	95-132 (NOL) ^a , 171 (Northrup-Carolina) ^b
Electrostatic Sensitivity	Fires >0.001 mfd 8 KV (NOL)
Density, g/cm ³	1.79 (NOL)
Vacuum Thermal Stability	1.26-3.5 cc/g/hr, 260°C (NOL)
Detonation Velocity, m/sec	7400 @ 1.76 g/cm ³ (NOL)
Heat of Detonation, Cal/g	845 (NOL)
Weight Loss, 48 hr, 210°C	negligible
Decomposition Rate, 500°F	0.2-0.3%/hr (NOL)
Size Range, μ	10-40 (NOL)
Cost per pound	\$600-700
Suppliers	Northrup-Carolina

Advantages Comparatively fair energy and heat resistance.

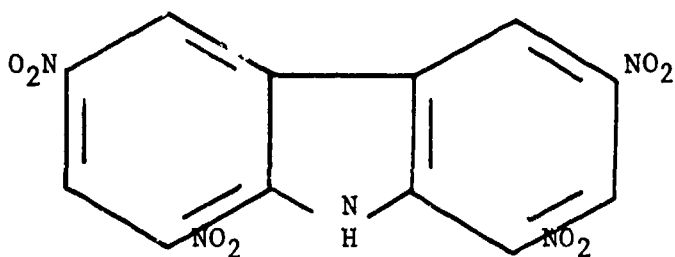
Disadvantages: Costly and unavailable, fine particle size.

References: Ref. 3, 4, 12, 15, 20, 21.

^a Composition B = 60 cm.

^b HMX = 65 cm.

TNC
1,3,6,8-tetranitrocarbazole



Autoignition Temperature, °C	310 (NWC)
Melting Point, °C	293-305 (NWC)
Impact Sensitivity, 50% Pt. cm	3/3 no fires or burns @ 79 cm burned at greater drop heights (NWC)
Friction Sensitivity	10/10 no fires, 440 kg-cm (NWC)
Electrostatic Sensitivity, 50% Pt.	1.41 Joules (NWC)
Density, g/cm ³	1.739 (NWC)
Vacuum Thermal Stability	0.07 cc/g/51 hrs @ 120°C (NWC)
Detonation Velocity, m/sec	No information available.
Heat of Combustion, Cal/g	3817 (NWC)
Size range, μ	18 μ mean diameter (NWC)
Solubility	Sol. hot acetone
Cost per pound	\$2.50 (1965)
Suppliers	Southern Dyestuff Co.

Advantages: Low cost, excellent availability, insensitive, could be recrystallized.

Disadvantages: Low energy, somewhat low melting point.

References: Correspondence, Southern Dyestuff Co. to B. A. Stott, 4-12-65.

At the time this project was undertaken, available data for heat resistant explosive candidates indicated TATB or TACOT to be the most feasible for immediate investigation. TATB, however, has the disadvantage of very small particle size and very poor loadability in castable formulations. Moreover, any attempts to recrystallize it to obtain a more favorable size distribution appear discouraging because of its negligible solubility in all common solvents. Although TACOT may be less promising from the standpoint of energy than TATB, possibilities of recrystallizing to larger size with resultant improvement in loadability might well compensate. Furthermore, the outstanding thermal stability of TACOT provides further recommendation for primary consideration.

Most preliminary screening studies with various binders were carried out with three different explosive fillers, TACOT, TATB, and DATB. The latter was included because of its comparatively low cost, relatively high energy and ease of recrystallization. However, in respect to heat resistance, its melting point at 275°C could put it at a disadvantage. Lead azide was excluded from immediate consideration because of handling hazards, tetranitrocarbazole because of unfavorable energy characteristics, and the two polyphenyls, NONA and DIPAM because of high cost and questionable availability. HNS was regarded as a possible replacement candidate for either TACOT or TATB. However, since its explosive properties were at the time relatively unknown, its thermal stability was inferior to that of TACOT, and it was more sensitive than many other explosives in its category, initial efforts were concentrated on TACOT and TATB with HNS to be studied at greater length if the former two should not prove feasible.

Solubility studies of TACOT indicate that this explosive will dissolve to a limited extent in a number of solvent systems. Results are described in Table 2. A similar survey has not been made as yet in the case of TATB; however, communication with its suppliers indicate much difficulty may be anticipated in attempting recrystallization. In the case of TACOT, dimethyl-sulfoxide appears to be one of the best solvents and a promising product was obtained by slow cooling and addition of hexane to a saturated solution of TACOT in DMSO.¹ Further work is needed to verify and optimize initial procedures.

In conducting the observations listed in Table 2, progressive attempts were made to completely dissolve TACOT in the specified solvent, first by warming, then by dilution. When appreciable solution occurred, crystals were obtained by slow cooling. These were then

¹ Process developed by M. Pakulak (Naval Weapons Center).

observed microscopically and in the case of DMSO were studied by differential thermal analysis in an attempt to determine whether degradation, adduct formation, or other modification had occurred. In several instances, namely pyridine, hydroxyethylmorpholine, and dimethyl formamide/nitrobenzene, the appearance and odor of the recovered product strongly indicated chemical interaction with the solvent. The DMSO or DMSO/hexane product, however, seemed to be unchanged except for physical size and shape.

TABLE 2. Solubility of TACOT in Various Liquids.

Solvent system	Concentration: TACOT/solvent				Appearance after cooling
	0.1 g/10 ml		0.1 g/20 ml		
	Ambient temperature	80 °C	Ambient temperature	80 °C	
Dimethyl Sulfoxide	Appreciably soluble.	Completely soluble.	Copious long, fine needles, orange, 200-300µ long, fragile.
Gamma butyrolactone	Very slightly soluble.	Appreciably soluble.	Very slightly soluble.	Complete solution.	Resembles original product.
Dimethyl Formamide/Toluene 1:1	Appreciable attack.	Formed cake.	Appreciable attack.	Nearly complete solution.	Rust-colored aggregates 0.01-0.03 inch diameter which break down to give fine powder < 1µ diameter.
Nitric Acid, 95%	Slightly soluble.	About 40% dissolved.	Slightly soluble.	Some residue.	Bright orange platelets, roughly hexagonal, very fine to > 180µ.
Pyridine	Slightly soluble.	Slightly soluble.	Slightly soluble.	Nearly complete solution.	Thin rust-colored needles, 20µ thick x 200-500µ long, discolored solvent, evidence of chemical change.
Hydroxyethyl morpholine	Appreciable attack.	Nearly complete solution.	Viscous and black. Obvious decomposition.
Dimethyl Formamide/Nitrobenzene 1:1	Appreciable attack.	Little change.	Appreciable attack.	Nearly complete solution.	Dark and tarry. Chemical reaction.
Dimethyl Formamide/CCl ₄ 1:1	Slightly soluble.	Slightly soluble.	Slightly soluble.	Slightly soluble.	Brick shaped aggregates of fine crystals plus powder < 5µ. Pronounced odor.
Dioxane	Very low solubility.	Very low solubility.
Benzene	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Nitromethane	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Diacetone Alcohol	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Cyclohexanone	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Methyl cellosolve	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Carbitol Acetate	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Mesityl oxide	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Trichloroethylene	Very low solubility.	Very low solubility.	Very low solubility.	Very low solubility.
Hexane	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.
Ethanol	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.
Tetrahydrofuran	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.
Chloroform	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.
Methylene Chloride	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.
Acetonitrile	Negligible solubility.	Negligible solubility.	Negligible solubility.	Negligible solubility.

BINDERS FOR HEAT RESISTANT EXPLOSIVES

A number of different types of castable, polymerizable resins and monomers were investigated for use with heat resistant explosive fillers. Included were polyesters, epoxies, unsaturated hydrocarbons, and silicones. A vinyl plastisol system was also examined in some detail because of its promising physical properties and convenient curing schedule. Fluorocarbons were considered but were not included in preliminary work because suitable types were not available commercially at the time.

Binders were evaluated in respect to the following considerations.

Processability. For adequate loadability viscosity should not be higher than that of Laminac EPX 147-2, the binder used for PBXN-101 and PBXN-102. Gel times should be reproducible and controllable within practical limits. Curing conditions should not be overly exacting and should not require or produce temperatures which might affect the stability of the filler.

Compatibility. The presence of the binder should not degrade the explosive. Combined filler and binder should exhibit as good thermal stability as the filler alone when subjected to autoignition, DTA, sensitivity, or vacuum thermal stability tests.

Heat Resistance. The binder alone should withstand temperatures up to the decomposition point of the explosive without severe gas evolution, burning, charring, liquefaction, or other serious degradation.

Physical Properties. The composition should cure with a minimum of shrinkage to a dense, reasonably strong solid, resistant to mechanical and thermal shock.

Various candidate binders were formulated and cured both alone and combined with the explosive fillers, DATB, TATB, TACOT, and in a few cases TNC. Loadability was limited to 40-60% filler because of unfavorable particle size distribution of the fillers. Satisfactory cured compositions were then evaluated and compared on the basis of their autoignition thermograms. Heat stability of the binders alone was determined by oven tests in which the material was heated in closed tubes at a rate of approximately 150°C per hour to a temperature of 380°C. Observations at 50° intervals and after cooling at the conclusion of the test revealed major decomposition characteristics. Very few formulations were found which could satisfactorily meet all the requirements described.

Two of the more promising, which contained TACOT with silicone binder, were scaled up from the preliminary 5-10 gram scale to 150-200 grams. These were cast without difficulty into 0.5-inch teflon molds, cured, and

sectioned into 0.75-inch lengths for measurements of detonation velocity and plate dent. HMX/silicone and TACOT/Laminac formulations were prepared as controls in order to more accurately compare the behavior of new explosive and binder with materials of better known characteristics.

EPOXY BINDERS

These varied in type from the conventional bisphenol A derivatives to the newer epoxy functional silanes. A few polyfunctional types such as Oxiron 2002 and allyl-epoxies were also investigated. In cases where high viscosity was a problem satisfactory dilution could usually be effected by use of either a low viscosity curing agent such as methyl nadic anhydride or a liquid amine, or a reactive diluent such as phenyl or allyl glycidyl ether.

Epoxy binders all exhibited one serious difficulty which rendered them unacceptable as high temperature materials. Autoignition tests on cured filled and unfilled compositions revealed the occurrence of severe exotherms at temperatures often as low as 160-230°C. This heat evolution, presumably the result of a secondary curing reaction, was usually sufficient to ignite the explosive filler and in a few cases even resulted in ignition of unfilled binder. Many of the epoxy materials were also quite hard and brittle and would probably require plasticization in order to withstand vibration and sudden temperature changes.

A summary of typical epoxy binders investigated is presented in Table 3.

POLYESTER BINDERS

Polyester resins in general are not noted for their resistance to extremely high temperatures. However, a few, usually modified by triallylcyanurate crosslinker, are reported to withstand exposures up to 500°F. Two sources were investigated, American Cyanamid Laminacs and Naugatuck Chemical Vibrin polyesters.

An initial test with Laminac EPX 147-2, a styrenated polyester used as binder for PBXN-101, revealed very poor heat resistance in combination with the three explosives DATB, TATB, and TACOT. Respective autoignition temperatures were 263, 276, and 256°C, thus representing decreases from 30 to 100° below the ignition points of the explosives themselves.

Vibrin resins 135 and 136A, polyesters modified with triallylcyanurate, were evaluated, both undiluted and thinned with various low viscosity monomers. Viscosity before dilution was unacceptable. Monomers tried as diluents included styrene, divinyl benzene, and diallylphthalate. Benzoyl peroxide or t-butylperbenzoate were used as initiators. In every case the resulting filled, cured compositions when subjected to thermal analysis showed pronounced exotherms at temperatures between 189 and

TABLE 3. Epoxy Binders Investigated for High Temperature Use with TACOT, TATB and DATB.

Name of material	Chemical structure	Curing agents used	Other additives	Advantages	Disadvantages
Shell Epon 815	bisphenol A derivative	m-phenylenediamine methyl nadic anhydride, BF ₃ complex, peroxides when applicable.	phenylglycidyl ether, Allyl glycidyl ether.	Good physical properties.	Diluent required. Autoignition with explosive 200-250°C.
Union Carbide ERLA 0510	p-aminoglycidyl phenol	Union Carbide 0812 and 0822 liquid amines, methyl nadic anhydride, tetrapropenyl succinic anhydride	Monsanto Modepox, polyallylglycidyl ether, GE Methylon	Good viscosity. Good physical properties.	Post-cure exotherms on heating to 230-270°C. Low autoignition values.
Union Carbide Unox 207X	dicyclopentadiene dioxide	Maleic anhydride	polypropylene glycol	Good viscosity.	Low autoignition values. Exotherms at 255 and 274°C.
Swift Epoxol 9-5	long chain poly epoxide of glycerol	methyl nadic anhydride	General Electric Methylon	Highly reactive. Used principally as acid scavenger & stabilizer.	Poor viscosity, questionable compatibility, premature exotherms.
FMC Corp. Oxiron 202	epoxidized polyolefin	methyl nadic anhydride, dicumyl peroxide.	ethylene dimethacrylate, phenyl & allyl glycidyl ethers, GE Methylon.	Multifunctional. Variety of formulations possible.	Diluent required. Unstable at high temperatures, low auto-ignition points.
Dow Corning Z6040	glycidoxypropyl trimethoxysilane	trimethoxysilyl propylethylene diamine (Dow Corning Z6020)	silane derivatives, ^a Dow Corning 6018	Extremely low viscosity.	Very weak. Resin needed. Questionable compatibility. Hydrolytic instability.
Dow Corning Z6077	1,3-bis (3 glycidoxypropyl) tetramethyl disiloxane.	methyl nadic anhydride, Shell curing agent CL	Very low viscosity. Good physical properties with curing agent CL.	Incompatible with explosives. Autoignition as low as 188°C.
Emerson-Cuming Eccomold L-266	Not known.	Catalyst 17 Emerson-Cuming.	Good physical properties.	High viscosity unless warmed. Low autoignition values.

^aSee section on silicone binders.

248°C, which were sufficient to ignite the test sample. In this case, as with epoxies, probably a secondary curing reaction is involved which liberates substantial amounts of heat.

Preliminary observations were carried out with Laminac resin 4232. This, like the Vibrin polyesters, is modified with triallylcyanurate. The material was highly viscous as received and was difficult to handle and dissolve in suitable monomeric thinners. Since previous work with other triallylcyanurate-based polyesters indicated serious stability problems after introduction of filler, further studies in this area were not continued.

VINYL PLASTISOLS

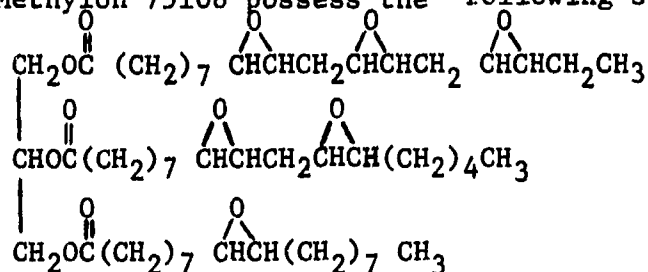
A brief survey was made to determine whether this type of system would withstand temperatures over 300°C when combined with explosive filler.

Plastisol systems offer a number of advantages. First, since curing is a physical rather than chemical mechanism, no hazardous exotherms from this source are anticipated. Also, curing times are generally very short. Furthermore, viscosity can be readily modified by addition of more plasticizer usually without too great a sacrifice in physical properties. The cured formulations are resilient, solid and very strong and tough, provided plasticizer content is not excessive.

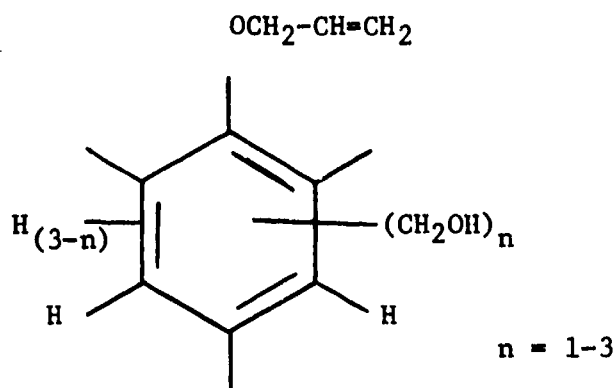
Two commercial materials were investigated, Union Carbide formulation QYLF/QYNL/ZKRA, and Watson Standard 21-726. The first was rejected on the basis of difficult processability and poor heat resistance; the latter showed some promise when compounded with TATB and a suitable stabilizer. However, oven tests on unfilled binders revealed liquefaction and degradation starting below 200°C.

Table 4 summarizes observations made on Watson Standard plastisols containing TATB filler. TACOT and DATB were also studied; however, in the case of these fillers autoignition results were inferior.

Watson standard 21-726 is polyvinyl chloride dispersed in phthalic ester. Santicizer S-141 is octyl triphenyl phosphate and Epoxol 9-5 and Methylon 75108 possess the following structures:



Epoxol 9-5



Methylon

The effect of Methylon in raising the autoignition point of TATB-filled compositions is interesting. Parallel results were not noted when either DATB or TACOT was used as filler. Autoignition tests only were performed on most of these formulations. Since physical consistency could therefore not be directly observed during the heating process, additional oven tests on binders alone may be of interest. The limiting factor in considering the PVC plastisol type of binders appears to be physical deterioration at temperatures considerably lower than the desired 500°F.

MISCELLANEOUS BINDERS

The following materials were screened with respect to high temperature compatibility with DATB, TATB, and TACOT.

Oxiron 2002 (Food Machinery and Chemical Corp.)

This is a polyfunctional compound containing unsaturated, hydroxy, ester, and epoxy groups. Viscosity without dilution was too high for good solids loading. Autoignition tests showed that heat resistance of filled compositions was too low to warrant further consideration.

Butarez CTL (Phillips Petroleum)

This resin is a carboxy terminated butadiene prepolymer. Like Oxiron 2002, it requires dilution or warming to achieve desired solids loading. Autoignition tests revealed that heat resistance was inadequate.

Methylon 75108 (General Electric)

This material was described in a previous section as an additive to stabilize PVC plastisol systems. It was also investigated as a component in epoxy and vinyl formulations. Alone it is too viscous to permit

TABLE 4. Plastisol Compositions Made With Watson Standard 21-726 and Triaminotrinobenzene Approximately 50% TATB. Cured 30-45 Minutes at 150°C.

Binder components	Respective ratio, %	Viscosity of binder	Cured appearance	Autoignition point, °C	Oven tests, binder alone
WS 21-726 unmodified ^a	100	Poor	Tough, flexible, solid.	254	180°C tacky, 200°C liquefied, fumes.
WS 21-726/S-141 ^b	50/50	Fair	Rubbery and flexible, softer and more flexible as S-141 increases.	227
WS 21-726/S-141/Epoxol 9-5 ^c	50/30/20	Needs improvement	Rubbery and flexible.	232
WS 21-726/S-141/PAGE ^d	50/30/20	Thin and fluid	Rubbery and flexible.	237
WS 21-726/DOP ^e /Methylon ^f	45/45/10	Fair to good	Excellent, tough and rubbery.	302-315	140°C exudation ^g 160°C liquefied
	50/30/20	Fair to good	Similar to above.	300-306
	40/40/20	Fair to good	Similar to above.	308
WS 21-726/DAP/DO ^h /Methylon with dicumyl peroxide	40/20/20/20 1.5% peroxide	Fair to good	Rubbery, weaker than preceding samples	309

^a Contains approximately 30% phthalate ester as received.

^b Octyl diphenyl phosphate, Monsanto Chemical.

^c Shell epoxidized glycidyl ester.

^d Polyallylglycidyl ether, Shell.

^e Dioctylphthalate.

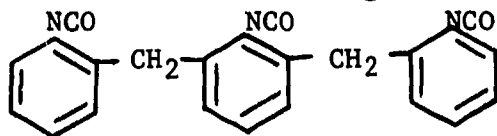
^f G. E. phenolic resin described in previous section.

^g A sample containing 21-726/Methylon 90:10 with no diluent showed only slight tackiness with no fumes at 200°C. Viscosity uncured was similar to that of unmodified 21-726. Testing above 200°C with or without filler was not carried out for this composition.

desired solids loading; therefore, a number of diluents were tried and resulting compositions were evaluated with respect to cured properties and stability. Included as diluents and comonomers were phenyl glycidyl ether, allyl glycidyl ether, styrene, glycidyl acrylate, polyallyl-glycidyl ether, diallylphthalate, ethylene dimethacrylate, Swift Epoxol 9-5, and octylene oxide. A variety of anhydride and peroxide curing agents were tried. Resulting products were all very brittle and showed questionable compatibility with the explosive fillers, either producing discoloration or autoignition exotherms as low as 160-200°C.

Polyurethanes

This type of binder is not especially noted for heat resistance. Some consideration was given use of the polyphenyl isocyanate, PAPI



as a nucleus for designing a more thermally stable structure. However, since it was felt that other types of polymers such as silicones would ultimately prove superior, experimental work was postponed.

FLUOROCARBON RESINS

Little work was undertaken in evaluating the feasibility of fluoropolymer/DATB-TATB-TACOT compositions for high temperature applications because of limited availability and high cost of suitable commercial monomers. Based on present knowledge and experience, fluorinated resins should be fairly heat resistant, especially if structures are selected to avoid dehydrohalogenation reactions.

To verify compatibility of explosive fillers with this general type of binder, autoignition tests were conducted on intimate mixtures of TACOT, TATB, DATB, and HNS with du Pont Viton A, a copolymer of vinylidene fluoride and perfluoropropylene.² The following results were obtained.

TACOT:Viton	350°C
TATB:Viton	312°C
DATB:Viton	287°C
HNS:Viton	325°C

² Test samples were prepared by dissolving Viton A in ethyl acetate, mixing the solution with explosive powder, and then removing ethyl acetate by evaporation.

Since the autoignition thermograms were typical of those for the explosive alone,³ complete compatibility is indicated and further investigation would appear to be warranted. Future effort should include attempts to prepare suitable monomers from available fluorinated intermediates.

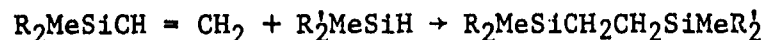
SILICONE BINDERS

For resisting high temperatures silicone resins are generally considered superior to all other conventional types. However, a number of problems involved in using them as binders for explosives delayed their consideration somewhat for the present project.

Commercially available silicone casting resins range from clear, fairly low-viscosity potting media to thick, heavy rubber prepolymers. Many of the former cure to form weak gels. The latter, while excellent from the standpoint of cured physical properties, are unacceptable in respect to initial viscosity and contain inorganic fillers such as iron oxide, calcium carbonate and siliceous materials. Curing of silicone resins may be effected by a number of mechanisms depending on the functional substituents attached to the siloxane backbone of the prepolymer molecule. Active groups, for example, may consist of epoxy, vinyl, isocyanate, or ether configurations which react upon the addition of suitable curing agents to form a solid polymer. Since results of earlier work with hydrocarbon systems had indicated limited stability in the case of some mechanisms such as epoxy, study of silicone polymerization was directed mainly toward three major types: vinyl addition, vinyl polymerization, and silanol condensation.

Vinyl Addition

These are two component systems consisting of polyfunctional vinyl and silane resins. Typical reaction involves the addition of silanic hydrogen to the double bond in the presence of a platinum catalyst.



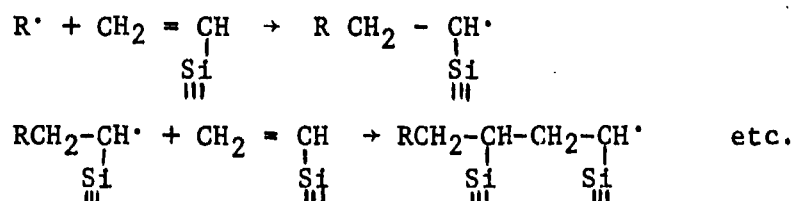
R and R' are long chain methyl siloxane groups with repeating vinyl and silane functionality.

³ DATB value is somewhat lower than that previously quoted because of different source and grade.

The reaction may be difficult to control and is sometimes subject to variation with changes in environmental conditions, especially in the presence of various additives such as explosive fillers. In these cases gassing as well as failure to solidify may result. Furthermore, commercially available products are either marginal or unacceptable from the standpoint of viscosity. A diluent is needed, which may further complicate the reaction and adversely affect curing rates and final properties.

Vinyl Polymerization

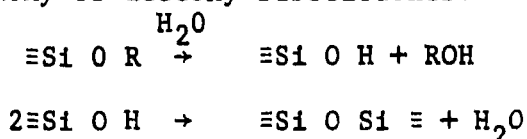
A limited number of resins and a fairly wide selection of silane monomers are available which contain ethylenic groups capable of polymerizing by free radical mechanisms of the type:



Theoretically, overly viscous resins could be diluted with reactive comonomers such as vinyl alkyl silanes or compounds such as styrene or diallylphthalate to obtain optimum viscosity and good cured properties. However, as in the case of vinyl addition, vinyl polymerization of silanic derivatives may be difficult to control in formulating explosive compositions. Silane diluents themselves are not readily polymerizable, often requiring severe conditions of heat and pressure. Furthermore, the reactivity of both diluents and resins is subject to retardation in the presence of explosive fillers, especially those containing nitro groups. Moreover, shrinkage and curing exotherms may constitute problems.

Condensation Polymerization

RTV rubbers are formed by the condensation of prepolymers containing alkoxy or acetoxy substituents:

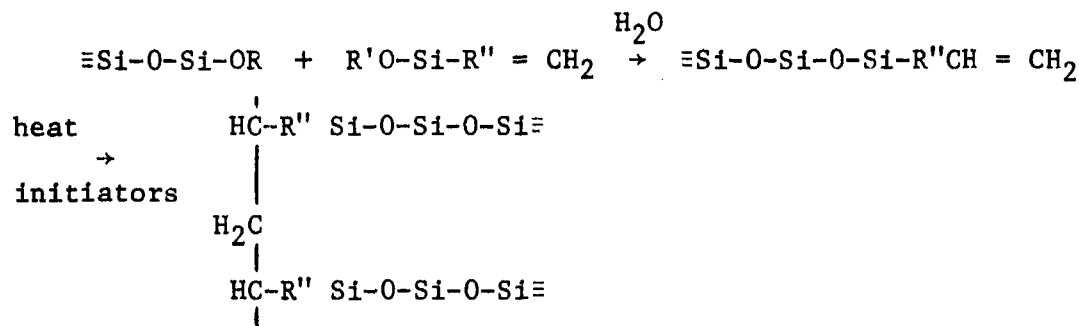


Hydrolysis occurs in moist air and curing may be accelerated by use of bases and heavy metal soaps such as lead octoate or dibutyl tin dilaurate. Reaction time is generally short, occurs at ambient or near-ambient temperatures, and may be affected by factors such as ambient humidity, size of casting, and design of mold. Furthermore, explosives such as DATB which contain primary amine groups may affect or enter into the curing reaction. Since volatile products are formed as a result of

silanol condensation, final castings may be porous if functionality is high and gasses cannot escape prior to solidification.

Combined Curing Mechanisms

Advantages of each type of cure might be realized and attendant difficulties minimized by combining functional types. For example, a polyfunctional diluent may react with an RTV rubber resin:



Initial viscosity is thus reduced, increased crosslinking may augment strength and resistance to thermal degradation, and porosity may be substantially lessened by selecting constituent ratios and curing schedules to permit gas evolving condensation reactions to be completed at lower temperatures before final vinyl polymerization has occurred.

Some fairly promising binders were obtained by the latter techniques. However, two major difficulties were encountered, namely: (a) excessively rapid gelation with high alkoxy contents and (b) tendency for vinyl containing diluents to volatilize rather than polymerize. Best properties resulted with a binder containing approximately 50% RTV resin diluted with both vinyl monomer and nonreactive polysiloxane fluid.

Results for Resin Types Based on Silane Addition

Detailed observations made on various commercial materials and modifications thereof are summarized in Appendix C, Table 11. These materials comprise chiefly the Dow-Corning Sylgard resins 182 and 184 and General Electric 615, all two-component systems. Most of the work was conducted with Sylgard 184 which was a representative type and comparatively low in viscosity.

Since viscosity as received, even in the case of the best resins, was marginal, three kinds of diluent were tried, inert polydimethylsiloxane fluids, vinyl silanes, and vinyl-alkoxy silanes. The first were not very effective in reducing viscosity. Furthermore, physical strength was lowered when enough was added for adequate thinning, and high temperature stability was impaired, with binder liquefaction occurring at temperatures over 300°C. This latter phenomenon may be attributed to the conversion of linear siloxane polymers to cyclic tetramers of relatively low molecular weight.

Vinyl and alkoxyvinyl silane diluents combined with Sylgard 184 at first appeared to produce promising compositions, especially with the explosive fillers TATB and TACOT. DATB filled compositions usually failed to solidify. Further investigation, however, showed that consistent results were very difficult to obtain in any case. Successful cures and subsequent stability were dependent on such environmental cures and subsequent stability were dependent on such environmental factors as mold configuration. Reducing the exposed surface area of the casting, for example, might result in gas evolution, discoloration, partial or complete failure to cure and other evidences of incompatibility. To overcome these difficulties several approaches were tried, including altering stoichiometric ratios of resin, curative, and diluent, precoating the explosive filler, and using non-silanic diluents such as styrene. In all cases, results were unacceptable, erratic and dependent on environmental factors. Binder alone cured differently from binder plus filler and evidence indicated the likelihood of competing reactions between various binder components and explosive fillers. Without fillers, cures were more consistent under all conditions. With filler, better cures were obtained under conditions of low humidity. Also, compositions containing the amino-nitro benzenes, DATB and TATB were stronger and tougher than those containing TACOT. It may be presumed, therefore, that in the presence of the former two compounds and the absence of moisture silanic addition of the two Sylgard components was favored, while the alkoxy diluent either reacted with the explosive filler or volatilized.

At higher ambient humidities, filled compositions tended to be porous, weaker, and tackier. In this case it is possible that the silanic hydrogen of the Sylgard curative was hydrolyzed, producing hydrogen gas, and the resulting silanol underwent condensation with the alkoxy diluent, leaving substantial percentages of unreacted vinyl resin and filler and under confined conditions, alcoholic byproducts.

Since Sylgard cures appeared difficult to control and condensable rubber resins at the time were showing more promise, work on the silane addition type was discontinued.

GENERAL ELECTRIC RTV 615. This material was very similar in behavior to Sylgard. Since it suffered from all the disadvantages of the latter besides having a higher viscosity, investigation was limited to initial examination only.

UNION CARBIDE Y-3466/3467. A three-component system comprising a methyl polysiloxane, Y-3467, a crosslinking agent containing silanic hydrogen, Y-3466 (L-31), and a metal soap catalyst, KL-1800, was tried alone and with the diluents vinyl triisopropoxy silane and divinyl tetramethyl disiloxane. Without diluent the resin was too viscous; however, compatibility with the three explosives, DATB, TATB, and TACOT appeared to be excellent, based on autoignition results. With or without diluent, gassing and subsequent porosity was impossible to control. Further work with this binder was therefore discontinued.

Silicone Resins Containing Polymerizable Vinyl Groups

Several proprietary resins were investigated as well as a number of low viscosity monomeric silanes. Results in general were very poor. Excellent, tough, solid polymers were frequently obtained on curing the binder alone; however, in the presence of the explosive filler curing was inhibited. Use of different curing agents and different comonomers failed to effect any improvement. The following formulations were studied:

UNION CARBIDE XR 65. This resin was too viscous as received. It was diluted with various monomers with the following results:

styrene	failed to cure with explosives
diallyl phthalate	failed to cure with explosives
divinyl benzene	milky, waxy and weak
tetraallyl orthosilicate	no cure with explosives
vinyl pyrrolidone	no cure with explosives
ethylene dimethacrylate	milky and tacky
glycidyl acrylate	milky and tacky
allyl glycidyl ether	sticky, tacky, incomplete cure
vinyl triisopropoxy silane	failed to cure with DATB and TACOT, TATB putty-like
allyl ethoxy silane mixture	discoloration and gassing with explosive filler
methacryloxy propyl tri-methoxysilane (Z-6030)	cured to firm consistency but auto-ignition results indicated incompatibility

DOW-CORNING R-7521. This is a low viscosity material which without filler can be cured at 125-150°C with dicup to produce a flexible polymer. Physical properties both alone and in combination with other monomers are very promising. An exceptionally strong, tough rubber was obtained by curing with two other components, vinyl triisopropoxy silane and Eccosil 4712A. However, in the presence of explosives either the compositions failed to cure or other incompatibility was evidenced by gassing, discoloration and low autoignition values.

DOW-CORNING R-7501. This resin is similar to R-7521 in its general behavior and properties but viscosity is higher, thus necessitating use of a diluent. In the absence of filler, promising cures were obtained with vinyl triisopropoxy silane, vinyl pyrrolidone, styrene, ethylene dimethacrylate and methacryloxypropyl trimethoxy silane. Questionable or unsuccessful products resulted when tetraallyl orthosilicate, diallylphthalate or Dow-Corning 1330 polydimethyl siloxane fluid were used. In the presence of explosive fillers failure to cure was observed in all

cases except with ethylene dimethacrylate and the methacrylate functional silane. However, the latter two compositions were incompatible in auto-ignition tests.

VINYL TRIISOPROPOXY SILANE. A number of different copolymers were tried but none offered sufficient promise to warrant continuing investigation. Either the formulation failed to polymerize or physical properties of the cured polymer were unacceptable.

METHACRYLOXYPROPYL TRIMETHOXY SILANE (Z-6030). Fair to good products were obtained both with 6030 alone and in combination with vinyl triisopropoxy silane, allyl ethoxy silanes, and vinyl trialkoxy silane. However, low autoignition results indicated questionable compatibility when DATB, TATB or TACOT were included.

RTV Rubbers

A number of RTV rubbers were investigated as heat resistant binders. The most successful were Dow-Corning Silastic 521 and Emerson-Cuming Eccosil 4712A. These were combined with several types of diluent and formulated with explosive fillers. The most promising were evaluated for thermal stability and explosive properties.

Commercial RTV rubbers are characterized by good strength and toughness, excellent flexibility and resistance to thermal shock, and superior heat stability. However, they possess a number of disadvantages for application as explosive binders. First, the viscosity is high and loadability is poor. This defect can be more or less overcome by the use of suitable diluents. Secondly, all resins supplied by commercial sources contain inert mineral fillers such as iron oxide or talc and have not been available in any other form. Again, use of diluents serves to overcome the effect of this filler on viscosity. However, such inert additives contribute in no way to the eventual end purpose of the formulation and only serve to increase weight and volume. Lastly, the condensation curing mechanism may be a potential source of difficulty due to the evolution of volatile by-products which in some cases might affect the stability of the final product as well as produce porosity and voids. However, most of the resins tested were of low functionality so that with careful selection of diluent and judicious control of curing rate condensation gases per se did not appear to offer too great a problem.

ECCOSIL 4712. Initial studies were carried out using the resin system Eccosil 4712A with Eccosil catalyst 4712D. These materials were originally part of a four-component formulation, Eccosil A-B-C-D, comprising respectively: an RTV silicone resin, a low viscosity epoxy, an epoxy curing agent, and a curative for the silicone. The epoxy constituents were found to be incompatible with explosive fillers and evidenced characteristics typical of those already described in the section dealing with epoxies. The silicone portion, except for its high viscosity,

appeared promising, with evidence of good compatibility and excellent physical characteristics on curing with explosive fillers.

To improve viscosity five types of thinner were investigated: (a) non-reactive dimethyl polysiloxane fluids, (b) alkoxysilanes, (c) unsaturated silanes, (d) vinyl or allyl-alkoxy silanes, and (e) unsaturated hydrocarbons. The best diluent systems were then tried with other RTV resins as substitutes for the Eccosil in an attempt to find an alternate source with low viscosity and equivalent or superior properties.

POLYSILOXANE DILUENTS. Several different silicone fluids were investigated as diluents for Eccosil 4712A/explosive compositions. These included materials of different viscosities and structures, some containing phenyl as well as methyl groups. A summary of results is presented in Table 5.

All formulations based on RTV resin with silicone fluids were characterized by very high autoignition points; in fact, the stability of the explosive actually seemed to be improved in the presence of the binder. Oven tests on the binder alone revealed that liquefaction occurs at temperatures over 300°C. This reaction, if endothermic or producing products of greater heat capacity, could account for the rise in auto-ignition point.

Polysiloxanes were not found to be optimum diluents: first, because of their physical instability below the decomposition temperature of TACOT, secondly, because they failed to reduce viscosity adequately unless used in high concentration, and thirdly, because their effect on physical properties was detrimental. As the percentage of diluent increased, compositions became very flexible and soft with low tear resistance. Phenyl siloxanes were not compatible with the Eccosil resin and separated out before or during curing.

Peroxides were incorporated in an attempt to produce crosslinks and thereby better physical properties and heat stability. However, little improvement was effected. Moreover, the peroxide appeared to introduce minor compatibility difficulties, lowering the autoignition point by 15-25°C and in some cases producing slight discoloration.

Cerium acetyl acetonate has been used effectively as a complexing agent to prevent high temperature cyclization of polymethyl siloxanes (Ref. 22). This approach has not been tried as yet in the present work. While it might result in improved heat resistance, the disadvantages of poor viscosity reduction and inferior physical properties would still have to be considered in modifying formulations with silicone fluids.

TABLE 5. Silicone Fluids as Diluents for Eccosil 4712A

Diluents	Ratio Eccosil: Diluent	Binder Viscosity	Appearance After Cure ^a	Oven Test Results, Unfilled	Autoignition With Filler, °C	
					TATB	TACOT
Dow-Corning 1330	10:7-9	mediocre	rubbery, flexible, relatively soft, low tear resist- tance.	320-330°C starts to liquefy. 340 liquid.	331	352
	10:9 ^b	mediocre	slightly stronger and harder than above.	310 fumes. 340 liquid.	317	335
Dow Corning 200	10:7.8 ^b	mediocre	flexible, solid, low tear resist- ance.	310°C fumes.	315	310
General Electric 910	10:9.3	poor	rubbery, somewhat elastic.	310-320°C fumes. 330 liquefies 340 liquid	335	344
General Electric SF 96(50)	10:13.8 ^b	poor	weak, porous.	290°C discolored 310 fumes 345 liquefaction	---	329
General Electric SF 96(100)	10:10.4 ^b	very poor	very porous, swollen.	---	---	---
General E Electric SF 1017 ^c	immiscible	---	---	---	---	---

^a 4712D, lead octoate, or dibutyltin dilaurate catalyst, 0.2% based on binder weight, step cured to 125°C from ambient in 48 hours.

^b 1.5% dicup in binder

^c Phenyl methyl silicone.

ALKOXY SILANE DILUENTS. A summary of results for this type of additive is shown in Appendix D, Table 12. In general these materials were excellent thinners when used in sufficient concentration, and strong, tough products with outstanding heat resistance were often obtained. Good compatibility with explosive fillers was indicated by high auto-ignition values. There was some evidence that the filler entered into the curing reaction, since the curing rate was faster and resulting compositions were usually harder and stronger in the presence of the explosives, in particular those with primary amine groups. Alkoxy silanes were somewhat difficult to use as sole diluents, however, because of their high reactivity. Some of the more highly functional ones, in particular, produced gelation almost immediately, and porosity in the final product was often a problem, presumably due to too rapid a curing rate with resultant entrapment of gases. This problem was overcome to a certain extent by reducing the concentration of catalyst, using step curing techniques, and incorporating a non-reactive co-diluent such as Dow-Corning 1330 fluid. Another difficulty involved control of ambient humidity. Since reaction rates and conceivably properties of final products could be influenced greatly by this latter factor as well as by moisture adsorbed on the surface of the explosive filler, additional, carefully controlled studies are needed to verify the practicality of employing high concentrations of alkoxy silanes as diluents in compositions of the type described.

Phenyl alkoxy silanes, like phenyl silicones, were as a rule incompatible with other binder components and formed a separate phase immediately on addition or during cure.

VINYL- AND ALLYL DILUENTS. Unsaturated silanes and unsaturated alkoxy silanes were investigated as thinners for Eccosil 4712A, alone and in combination with inert silicone fluids such as Dow-Corning 1330. The former type of diluent appeared promising both from the standpoint of viscosity reduction and final cured properties. However, difficulty was experienced in consistently obtaining adequate vinyl polymerization. Preliminary results for some of these formulations are summarized in Appendix E, Tables 13, 14, and 15.

Properties of Eccosil 4712 cured with unsaturated silanes were variable, ranging from porous, weak structures to extremely tough, solid compositions. Shrinkage, also, appeared to vary considerably. Most successful results were obtained with sym.-divinyl tetramethyl disiloxane as a diluent. Vinyl triisopropoxysilane and allyl ethoxy silane also produced strong, solid rubbers when combined in various ratios with Eccosil 4712A. In most cases inclusion of DC 1330 or comparable silicone fluid as co-diluent was advantageous in raising the autoignition point, and with the alkoxy vinyl derivatives, in controlling the curing rate. Inferior physical properties and exudation above 300°C resulting from the presence of the silicone fluid could be minimized by keeping its percentage below 15-20%.

Difficult polymerizability of unsaturated silanes in general indicated the advisability of employing fairly rigorous curing conditions. Therefore, in initial work all formulations were carefully degassed and coated with a layer of paraffin to exclude air. Also peroxide curatives were incorporated along with the catalyst 4712D so that vinyl polymerization as well as condensation reactions would be promoted. As the investigation proceeded, it was noted that all formulations containing compounds with ethylenic double bonds, including both silane and straight hydrocarbon derivatives, were characterized by abnormally low autoignition points. In the case of TACOT filler, the autoignition temperature was reduced 40-60° below that of the explosive alone. With TATB, the reduction amounted to about 20-30°, while DATB with a much lower decomposition point initially, remained relatively unaffected. Elimination of variables proved that two factors were responsible for the apparent incompatibility: the paraffin used to coat the surface and the peroxide curative. The latter lowered the autoignition point by 12-25°C. Paraffin, although apparently immiscible and inert when tested by itself, reacted with the formulation or with a control sample of explosive alone to cause ignition at temperatures as low as 285-290°C. Typical thermal data are presented in Table 6. When the two detrimental factors were eliminated, further verification with a number of different vinyl compounds showed autoignition points comparable to those obtained with alkoxy diluents, with only a few minor variations resulting from the effect of the particular structure involved.

Scale-up of the best binder formulations based on Eccosil 4712 plus vinyl diluent filled with either HMX or TACOT revealed a serious problem not detected in the small scale preliminary evaluation. Densities were low and chemical analysis of the cured material failed to agree with that for uncured composition or with nominal values. Also, diameter measurements of cured cylinders showed considerable shrinkage. All these inconsistencies were far greater than would be expected from silane condensation alone. Further investigation indicated that a substantial percentage of the unsaturated diluent was being lost through volatilization during the curing stages, 80-125°C.

Table 7. lists such losses for a number of different monomers examined quantitatively under comparable conditions. While in some cases high losses were characterized by porosity, in others, such as divinyl tetramethyl disiloxane, there was no visible indication even at 30X magnification. Specimens appeared solid, dense, and tough. Diameters, however, decreased from a nominal 0.500 inch to 0.45-0.46. Volatility did not appear to be solely a function of vapor pressure of the diluent alone.

Attempts to correlate diluent structure with the tendency to volatilize rather than polymerize showed that allyl and vinyl functionality behaved in general similarly. Increasing the number of unsaturated substituent chains reduced volatility. For example, the tetrafunctional

TABLE 6. The Effect of Paraffin^a and Peroxide^b on High Temperature Stability of TACOT/Silicone Compositions

Formulation	Autoignition Point, °C			
	No Dicum/ No Paraffin	Paraffin	Dicum	Paraffin + Dicup
Paraffin alone	...	Melts 50-55°C. No other reaction to >350
TACOT, as received	350-360	290
TACOT/4712-silicone fluid ^c	361	335-340	350	339
TACOT/4712-silicone fluid-alkoxysilane	366	302
TACOT/4712-vinyl silane	360	330	350	295
TACOT/4712-silicone fluid-vinyl silane	365	298-305	349	...
TACOT/4712-vinylalkoxy-silane	362	318	347	303
TACOT/4712-vinylbenzene	329	299-310

^a Used to exclude air during vinyl cures.

^b Curing agent for vinyl polymerization and crosslinking.

^c Polydimethyl siloxane diluent.

allyl was least volatile in the series: $(\text{Al}10)_4 \text{Si} < (\text{Al}10)_3 \text{Vi Si} < \text{Al}1 \text{ or Vi (OR)}_3 \text{Si} < \text{Al}1 \text{ or Vi Me}_3 \text{Si}$. Also, $\text{Al}1_2 \text{Me}_2 \text{Si}$ was less volatile than $\text{Al}1 \text{ Me}_3 \text{Si}$. Increasing alkoxy chain length reduced volatility as, for example, in the series $\text{Vi}(\text{Al}10)_3 \text{Si} < \text{Vi}(\text{IPrO})_3 \text{Si} < \text{Vi}(\text{EtO})_3 \text{Si}$. While relative vapor pressures may have some bearing on observed volatility, that this is not a complete explanation is evident by examination of boiling point values in Table 7.

In attempts to reduce volatility, the following modifications were tried:

- Altering the concentration and type of curing agent,
- changing the curing schedule,
- curing in a nitrogen atmosphere,
- curing in a closed container under slight pressure (up to approximately 1.25 atmospheres),
- substituting polydimethyl siloxane fluid for part of the monomeric diluent.

These variations were studied with divinyl tetramethyl disiloxane, tetra-allyl orthosilicate, styrene, and divinyl benzene. With the latter and methyl polysiloxane fluid in the binder, it was possible to reduce losses to 0.1% or less based on total binder.

In respect to catalyst, the mixed peroxides, 1% each t-butyl perbenzoate/dicumyl peroxide, were found most efficient. Increasing the concentration of 4712D reduced volatilization to a slight extent but not sufficiently to compensate for the pot life problems involved. A step cure from ambient to 60 to 80 to 125° was superior to direct curing at 125° only, and curing with nitrogen under pressure effected slight improvement.

Compositions satisfactory for measuring detonation properties could be obtained with a binder comprising either 10:8:2 or 10:5:5 4712D silicone fluid/divinyl benzene respectively cured with the mixed peroxide as indicated. With these formulations it was possible to obtain a reasonably dense and non-porous filled composition with little shrinkage and weight loss in cure and with good strength and resiliency. Extensive evaluation of thermal resistance was not carried out for this type of binder; however, the following autoignition points were observed with various explosive fillers:

HMX	252°C	TATB	325°C
DATB	303	TNC	329
HNS	296	TACOT	329

The low value for TACOT, compared with its autoignition point of 350-360°C, may be attributed to the peroxides in the composition.

TABLE 7. Volatility of Diluents Cured With Eccosil 4712 A/D

Eccosil/Diluent 5:4 Pts. by wt. 1% each tBPB/dicup. Step-cured to 125°C

Diluent used	Diluent BP °C/mm ^a	% wt. loss on curing ^b	Consistency after curing
All Si Me ₃	83/705	41.5	Very porous.
Vi Si Me ₃	56/706	36	Porous but tough.
Vi Si (OMe) ₃	123/760	35	Failed to solidify appreciably.
ATFA	73/710	32	Extremely porous.
All ₂ Si Me ₂	135/712	29	Tacky, highly elastic.
(Vi Si Me ₂) ₂ O	136/704	20-30	Tough, rubbery, appears solid.
α Me styrene	162/760	19	Weak, nonhomogenous, partly liquid.
All Si (OEt) ₃	175/760	13.2	Tacky, weak, porous.
Vi Si (OEt) ₃	158/760	12	Porous but tough.
All ₂ Si (OEt) ₂	190/741	11	Tacky, elastomeric, fairly strong.
Vi Si (OAll) ₃ + Si (OEt) ₄ ^c	90.3/7.5 166/710	11	Porous, somewhat weak.
All ₃ Si (OEt)	202/760	9	Tough but porous.
Vi Si (OIPr) ₃	170/760	8	Tough, solid, strong.
Vi Si (OAll) ₃	90.3/7.5	6	Fair strength, slightly porous.
Si (OAll) ₄	135/35	5	Tacky and weak, hardening on aging.
Vinyl benzene (styrene)	145/760	5	Solid and tough, a few large voids.
Divinyl benzene	polymer- izes 135- 150/710	0.6	Hard and solid. Thin film orange crust on surface.

^a Approximate in some cases. Taken from literature or determined by micromethod.^b 44% theoretical maximum if all diluent volatilized.^c 4712A - 55%, alloxysilane - 39%, ethyl silicate - 6%.

SUBSTITUTE FOR ECCOSIL 4712A. While Eccosil 4712A was being evaluated with various diluents, a search was made to find alternate, possibly more suitable resins with similar chemical structure and properties. A number of silicone rubbers were examined and their behavior in explosive compositions was compared. Included were: General Electric resins RTV 11, RTV 60, RTV 411⁴ and RTV 560⁴, Dow-Corning Silastic RTV 850, 589, 601, 521, and S5346, and Sylgard 51 Dielectric Gel.

Suitability was judged by viscosity as received and after dilution, curability, compatibility with explosive fillers, consistency on curing, and heat resistance. Thinners used in evaluating were Dow-Corning 1330, divinyl tetramethyl disiloxane and vinyl triisopropoxy silane. Silastic RTV 521 appeared to be the best choice as a substitute for the Eccosil material, showing excellent thermal stability and good properties in general except for considerable shrinkage during cure.⁵

ENERGY CHARACTERISTICS OF TACOT/SILICONE COMPOSITIONS-COMPUTED VALUES⁶

Because of the relatively low energy of high temperature explosive fillers, it was not anticipated that any of the heat resistant candidates would be capable of extremely high damage potential compared with compositions such as PBXN-101. Added to the inherent deficiencies is the experimental difficulty of obtaining high loadability with fillers of unsuitable particle size and inert binders of relatively high viscosity. Accordingly, some consideration was given the possibility of including additives such as dense perchlorates which might contribute to detonation energy. Not only should such compounds be favorable in respect to detonation reactivity; many of them are, in addition, readily soluble and could therefore be recrystallized to a particle size which would improve overall filler loadability. Examples of such additives are listed in Table 8.

COMPUTED VALUES

In attempting to predict roughly which type of system and which additives would be feasible, a computer program was carried out on a limited basis to establish detonation parameters by means of the Ruby code. Such computations in past work with C-H-O-N systems have shown excellent correlation with experimental results (Ref. 23). However, in

⁴ Phenyl methyl silicone.

⁵ Later results showed this to be due to diluent volatilization during cure, as with 4712A.

⁶ Acknowledgements are due A. J. Dierolf and I. Kurotori for assistance with this section of the report.

the present instance, predictions are more subject to doubt. The behavior of compounds containing elements such as silicon or metals is uncertain at the temperatures and pressures of detonation, assumptions must be made regarding possible products and their thermodynamic states, and experimental evidence is lacking which might be used to make corrections or substantiate any assumptions. It is therefore not possible to predict with any degree of certainty at the present time either the comparative effect of different additives or even the concentration effect of any one additive. However, the accumulation of experimental data should prove valuable in providing greater insight into the mechanisms involved. High temperature compositions provide a fertile field for such investigation since they may involve a variety of structures and components which have not yet been encountered in more conventional explosive systems.

Ruby calculations have been performed on silicone-based systems with the explosive fillers, TACOT, TATB, TNC, and HMX.⁷ Predicted detonation velocities for the high temperature candidates fall between 6300-6700 meters per second at the 15% binder level, with TATB and TACOT the most promising and TNC inferior. This is in accordance with expectations based on somewhat fragmentary experimental evidence. Theoretical computation also indicates an energy loss when siloxane is substituted for hydrocarbon polymer. This again agrees with observed values. For example, Ruby calculations predict.

	ρ	DV	P
HMX/Laminac 82/18	1.694	8016	275
HMX/Silicone 83/17	1.61	7481	205
HMX/Silicone 85/15	1.69	7719	226

Results for the latter two silicone compositions may be significantly affected by which, as yet questionable, thermodynamic variables are selected in performing the computations. However, the effect of silicone substitution is noteworthy and in good general agreement with experimental evidence shown in the next section (Table 9) for comparable formulations.

Formulations have not yet been prepared experimentally which contain a dense oxidant with TACOT or TATB and a silicone binder. However, the following additives have been examined on a theoretical basis: sodium perchlorate, lithium perchlorate, potassium perchlorate, sodium azide, sodium peroxide.

The effect of each of these compounds in a TACOT/silicone system was computed by Ruby code and the results for various compositions entered

⁷ Reported in memoranda: I. S. Kurotori to A. J. Dierolf, Feb-Mar, 1965, Reg. 4535-131-65 and 4535-114-65 and A. J. Dierolf to B. A. Stott, April 1966, Reg. 4541-187-66.

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TABLE 8. Potential Additives for High Temperature Explosive Compositions^a

Compound ^b	Melting or transition point, °C	Decomposition point, °C	Density, g/cm ³	ΔH_f KC/mole	Remarks
Perchlorates					
LiClO ₄	236-239	410-430	2.429	-90.38	Low melting point detrimental
KClO ₄	610	>400	2.52	-103.6	Very heat stable
NaClO ₄	...	482	2.02	-92.18
TlClO ₄	501	...	4.89	...	Toxic. Good density
Ba(ClO ₄) ₂	505	>500	3.2	-192.8	May have a low transition point
Chlorates					
Hg(ClO ₃) ₂	4.998	...	Good density, data scarce
Peroxides					
Na ₂ O ₂	...	460	2.805
Cs ₂ O ₂ , Cs ₂ O ₄	400	-O ₂ , 600	4.25	...	Good density and stability
BaO ₂	450	-O, 800	4.96	-150.5	Good density and stability
Periodates					
KIO ₄	582	-O, 300	3.62	...	Low decomposition point
NaIO ₄	...	300	3.87	...	Low decomposition point
CsIO ₄	4.259	...	Inadequate data
LiIO ₄	Inadequate data
Ba(IO ₄) ₂	Inadequate data
Ce(IO ₄) ₄	Inadequate data
Iodates					
Ce(IO ₃) ₄	Inadequate data
Pb(IO ₃) ₂	...	300	6.155	...	Good density, low decomposition point
Hg(IO ₃) ₂	Inadequate data
Miscellaneous					
LiNH ₂	380-400	>430	1.178	-43.5	Heat resistant, energy contribution doubtful
NaN ₃	...	385-388 ^c	1.85	...	Heat resistant, energy contribution doubtful
KN ₃	350	400 subl.	2.04	...	Heat resistant, energy contribution doubtful

^aData are conflicting for many of these compounds. Values were obtained from many miscellaneous sources and need to be confirmed. Principle sources were Refs. 5, 24, and 25, and manufacturers' data.

^bThose listed are available commercially.

^cAutoignition point.

on triangular simplots to permit graphing isometric contour levels of density, detonation velocity, and peak pressure.⁸ The following trends were indicated at the 15-20% binder level:

1. Substitution of alkali metal perchlorates for part of the TACOT may improve both velocity and pressure.
2. Sodium peroxide may offer some improvement at higher levels of substitution (25-30% Na_2O_2), but is generally inferior to the perchlorates.
3. Addition of sodium azide is detrimental to explosive properties.

Future experimental verification of these predictions should prove interesting.

EXPERIMENTAL RESULTS

Earlier test results obtained under another program⁹ with formulations based on HMX/Sylgard 182, 85:15 respectively, indicated comparatively low detonation velocity values. For example, a composition containing this silicone binder showed a velocity of 7760 meters per second, while a control with the same HMX loading but containing a hydrocarbon polyester averaged 8150. It was hypothesized that this difference was due to the siloxane bond structure which, because of either unfavorable kinetic or thermodynamic decomposition characteristics, acted as an "energy sink" during the detonation process.

To verify this observation scale-up was attempted with the two most promising RTV resins, Eccosil 4712A and Dow-Corning RTV Silastic 521. Divinyl tetramethyl disiloxane was used as a thinner and 150 gram batches were prepared containing 80% nominal HMX, a standard explosive of known behavior. Two additional batches were also prepared with TACOT as a filler. Only 60% loading was attempted in the latter case because of the small particle size of the explosive. The compositions were successfully mixed under partial vacuum, cast into molds 0.5-inch diameter by 3.0-inch high, and cured to solid cylinders with good strength and resiliency. Preliminary data for these compositions are presented in Table 9.

When low densities and low binder analysis prompted an investigation leading to the detection of excessive diluent loss during cure, an additional batch was formulated based on divinyl benzene/polysiloxane as a

⁸ In performing thermodynamic computations major metallic detonation products were considered incompressible, SiO_2 (liquid), compressible C (solid), K_2 (gas), KCL (gas), LiCl (gas), and Li_2O (gas). These assumptions have not been confirmed by kinetic studies.

⁹ Condor explosive development under contract RM3731-001/216-1/W107-00-01.

TABLE 9. Properties of 150-200 Gram Formulations Containing Silicone Binders with HMX or TACOT.

Composition	Respective nominal percentages	Analyzed ^a % binder	Processability	Cured appearance	Density g/cm ³	Auto-ign. °C	Sensitivity		
							Impact ^b 50% pt.	Friction ^c	Electro-static
HMX/Eccosil 4712A/divinyl tetramethyl disiloxane/4712D	80.0/11.2/8.6/0.04	19.5 uncured 12.4 cured	Very thin and fluid but thickened during mixing.	Slight shrinkage, solid, resilient. 30X - no visible voids.	1.641	225-258	25	1,240 pounds 50% point	10/10 no fires at 12.5 joules
HMX/RTV 521/divinyl tetramethyl disiloxane/521 catalyst	79.6/11.1/8.8/0.5	20.2 uncured 13.1 cured	Good loadability but thickened during mixing.	Similar to above. Slight shrinkage, solid, no visible voids.	1.640	260	24	1,230 pounds 50% point	10/10 no fires at 12.5 joules
HMX/Eccosil 4712A/DC20/DVB	80/10/8/2	19.8 uncured 18.8 cured	Good. Readily castable.	Solid, no visible voids, resilient.	1.669	252	23	10/10 no fires at 1,000 pounds	10/10 no fires at 12.5 joules
TACOT/Eccosil 4712A/divinyl tetramethyl disiloxane	59.4/22.7/17.8/0.07	38.7 uncured 27.0 cured	Initial viscosity good but thickened during mixing.	Considerable shrinkage, solid, resilient, firm, fair strength. 30X - no voids.	1.339	350	Partial burn at 250-300 cm	10/10 no fires at 1,800 pounds	10/10 no fires at 12.5 joules
TACOT/Eccosil 4712A/divinyl tetramethyl disiloxane	59.4/22.7/17.8/0.04	39.7 uncured 26.8 cured	Reduced catalyst slowed gelation. Fluid and readily cast.	Considerable shrinkage, solid and resilient. 30X - some blow holes and cracks.	1.286	---	---	---	---

^aThe difference between nominal and analyzed binder is suspected to be due to loss of volatile constituents during mixing and curing.^bComposition B = 36 ± 3 cm.^cABL sliding friction. 75/25 cyclool fires at 700 pounds (50% point).

diluent. Appearance of this composition resembled that of the first series, with the difference, however, of higher density and higher analyzed binder content, more nearly corresponding to the nominal value.

Detonation velocity and plate dent measurements for these compositions are shown in Table 10 together with analogous results for HMX/polyester controls containing no silicone. At equivalent nominal compositions, the silicone/vinyl disiloxane show the lowest velocities and dent values. The silicone/polysiloxane/divinyl benzene results are somewhat higher due possibly to a less porous microstructure, higher density, and a slightly lower silicone content (10% DVB in binder). All values are significantly lower than those for corresponding non-silicone controls. As further confirmation, additional results are included for the earlier Sylgard work. Binders containing siloxane linkages do appear to be energy sinks, as previously suspected, at least as far as detonation velocity is concerned.

TABLE 10. Comparative Values for Detonation Velocity and Plate Dent.
HMX With Polyester and Silicone Binders.

Binder	% HMX		Density, g/cm ³	Diameter, in.	Detonation velocity m/sec	Plate dent, in.	Remarks
	80	85					
Polyester Laminac EPX 147-2	80	80.2	1.676	0.50	7,893	0.082 - 0.085	PBXC-112. Information furnished by H. Stanton, J. Whitson. Low density and high analyzed filler due to VDS volatilization on curing. No visible voids - 30X. Low density and high analyzed filler due to VDS volatilization on curing. No visible voids - 30X. Substitution of less volatile diluent resulted in higher density. Explosive measurements still inferior to those of polyester although densities essentially same. This information furnished by C. W. Falterman and D. Sbrocca under contract, RM 3731-001/216-1/W107-00-01.
	82	82	1.679	1.625	7,980	0.28	
	85	84.4	1.701	0.50	8,167	0.084 - 0.087	
	85	85.7	1.699	1.625	8,148	0.31	
Silicone Eccosil 4712/VDS 1:1.2:8.8	80	80.5	1.647	0.50	7,447	0.080 - 0.084	
		87.6 ^b					
Silastic 521/VDS 1:1.1:8.8	80	79.7	1.639	0.50	7,374	0.079 - 0.082	
		86.9 ^b					
Eccosil 4712/DC 20/DBV 10:8:2	80	80.2	1.674	0.50	7,624	0.077 - 0.081	
		81.2 ^b					
Sylgard 182/DC - 200 110:35	85	85.3	1.669	1.625	7,761	0.293	

^a On uncured sample unless otherwise noted.

^b Cured sample.

NOTE: The TACOT/silicone compositions described in Table 14 were not detonable because of high inert binder content and low density due to diluent volatilization. However, at these binder levels (40%), HMX at 0.5-inch diameter is also borderline in detonability.

SUMMARY AND CONCLUSIONS

Studies both at the Naval Weapons Center, China Lake, and Naval Ordnance Laboratory, White Oak, have shown that a number of explosives potentially suitable as fillers in castable compositions can withstand high temperatures-over 250-300°C-without sudden or extensive decomposition. TACOT was found to be very stable, with an autoignition point exceeding 350°C. TATB and HNS were comparable, igniting at somewhat lower temperatures but still above 300°C. Other new compounds such as DIPAM or NONA may also offer considerable promise. However, the latter are still more or less laboratory items and production quantities at reasonable cost do not appear at all imminent.

Unfortunately little information is available as yet concerning detailed explosive properties of many of these new heat resistant materials. Existing evidence indicates that they are all significantly inferior to HMX or RDX in destructive capability. With optimum formulation, it is doubtful that compositions can be made which will show detonation velocities better than 6000-6500 meters per second. Even to achieve this range, filler loadability will have to be high, with filler particle size optimum and binder viscosity low.

Of the explosives tested thus far in the laboratory, TACOT appears to offer the greatest promise. HNS, however, which may be eventually more feasible from the standpoint of cost, availability, and susceptibility to size modifications, has not been evaluated experimentally at this Center. Like TACOT, its energetic potential does not appear outstanding. TATB is costly and very difficult to recrystallize to modify particle size, while DATB and TNC are less heat resistant and the latter is comparatively unenergetic.

Binders which were the most heat resistant and most compatible at high temperatures with explosive fillers were based on silicones. Much difficulty was experienced curing silicone monomers with ethylenic unsaturation in the presence of nitro compounds. However, products with good physical properties were obtained through silanol condensation, with vinyl or alkoxy silanes and nonfunctional polysiloxanes employed to obtain the desired viscosity. RTV rubber resins, Eccosil 4712A or Dow-Corning silastic 521 could be diluted with materials such as vinyl triisopropoxysilane, divinyl benzene, or methyl polysiloxanes to permit filler levels with HMX of 80% or higher. After curing, resulting products were tough, solid, resilient and heat resistant. Some difficulty was experienced with excessive diluent loss during cure, with attendant shrinkage and weight loss.

Detonation velocity and plate dent measurements revealed that the type of binder most attractive in respect to thermal stability might be detrimental in its effect on explosive properties. Compositions made

with binders containing Si-O linkages were found to have detonation velocities significantly lower than those made with hydrocarbon binders such as the unsaturated polyester, EPX 147-2. Since the potential energy of currently feasible heat resistant systems is already low because of the low energy filler, it would seem inadvisable to further augment this deficiency by using a binder which acts as an "energy sink." A possible means of reducing or eliminating the difficulty might be more extensive dilution of silicone with non-siloxanes such as divinyl benzene or vinyl silanes or complete substitution of the siloxane polymer backbone with a chain comprising Si-C or Si-N linkages. In the former instance curing of the diluent might be difficult since current results have shown a tendency for many vinyl additives to volatilize rather than polymerize. In the latter case, both Si-C and silazanes would be expected to have poorer overall stability than siloxanes and probably would be difficult to obtain as low viscosity liquids.

Fluorocarbons, although less heat resistant than silicones, are stable to temperatures close to the decomposition points of the fillers. Furthermore, this type of structure is compatible with most explosives and low viscosity monomers are becoming increasingly available. Initial results indicate that this type should be investigated further.

Epoxies, polyesters, polyurethanes and PVC plastisols were either insufficiently heat resistant or were incompatible with explosive fillers at temperatures well below their autoignition points. Epoxies, in particular, exhibited exothermic reactions on heating to temperatures of 160-230°C. When the binder was combined with explosive filler, these exotherms were sufficient to cause immediate and in some cases violent decomposition.

A limited number of Ruby calculations were made to predict the relative efficiencies of various binder systems and additives. Because of assumptions required in non - C-H-O-N systems and lack of experimental verification to back them up, due caution must be exercised in using computed predictions at the present time. However, computations agree with experiment in predicting an energy loss resulting from use of siloxane configurations. Calculations indicate that some advantage may be gained in including dense oxidants in TACOT/silicone formulations. Such additives, because of their more favorable size characteristics, should, when substituted for part of the explosive filler, provide higher solids loading and better processability.

SUGGESTIONS FOR FUTURE WORK

Future needs fall into three general areas: Improvement of the explosive filler, the heat resistant binder, and the system as a whole.

New high temperature explosives are continuing to be synthesized at the Naval Ordnance Laboratory, White Oak, and elsewhere; it is possible that a fortuitous breakthrough could at any time provide a better filler material than those presently available -- one with higher energy, superior heat resistance, and better processability. Promising candidates should continue to be examined in both castable and compressible formulations.

With respect to existing products such as TACOT, TATB, or HNS, methods are needed to modify particle size so that maximum loadability may be realized. The latter explosive should also be examined in combination with some of the more promising binders found incompatible with TACOT or the amino nitrobenzenes. A modification in filler chemical structure could presumably eliminate some of the curing difficulties encountered with resins such as Dow-Corning R-7521 which appeared promising in many other respects but failed to polymerize in the presence of explosive fillers thus far investigated.

One possible approach to obtain high explosives loading with good processability and ultimate high stability might involve the attachment of functional groups to low melting explosive compounds so that they would be capable of reacting with binder materials on curing to form a crosslinked structure. In this way, candidates which would normally be limited by their low melting points could be irreversibly cured to solid consistency with the low melting point an asset as far as processability and castability were concerned. Compounds based on the fluoro-nitro-benzene structure might fall into this category.

In respect to high temperature binders, both immediate and long-range approaches may be profitably employed. In the former category it should be possible to develop reasonably stable systems based on fluoro-carbon monomers with a minimum of time and effort. This type of compound is generally compatible with explosive fillers and might be capable of providing a castable composition with heat resistance equivalent at least to that of PBXC-8. Any new products developed should be evaluated at higher temperatures not only in respect to chemical stability but also for physical strength and performance.

Another short-range approach would entail successive replacement of siloxane diluents in the Eccosil system with reactive hydrocarbon diluents and determining the effect both on energy and heat resistance. Compositions studied quantitatively thus far have contained binders which were either entirely or predominantly silicone, for example Eccosil 4712A/

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VDS/1330 or 4712A/DVB/DC20 containing 10% hydrocarbon. Substitution of DVB for all of the DC20 and increasing the overall percentage of diluent should improve both detonation velocity and binder viscosity. Preliminary experiments have indicated that ratios as high as 5:4 Eccosil/DVB may be cured with less than 1% weight loss to give strong, homogeneous consistencies. The effect on explosive properties of varying the concentration of siloxane in the binder should be interesting to observe and should contribute information which might be useful in attempts to correlate theoretical predictions with experiment.

As a longer range project other silicone structures can be studied including the silazanes, Si-N, and lesser known configurations involving elements such as metals bonded with silicon. Other types of compounds which show promise and should be examined concurrently include such structures as triazines, polyamines, polyimidazoles, carboranes, polyesters, metal organics, and highly fluorinated chains. The main problem in employing materials such as these will be devising a means of making the formulation castable since the basic monomeric units for starting materials are generally solids with fairly high melting points.

Lastly, there are a number of additives or co-fillers which might be considered both in computer and experimental programs. For example, high melting, very heat stable, heavy metal perchlorates are available which should contribute both to oxygen balance and density. These could be evaluated in the systems currently described as well as in future formulations.

APPENDIX A

PREPARATIVE PROCEDURES

For preliminary evaluation, binders were first hand-mixed on a 5-10 gram scale, then blended with each explosive and cured in cylindrical teflon molds, 0.5-inch I.D. Filler loadings averaged 40-60% in most cases depending on explosive particle size and binder viscosity. After curing, compositions were examined for porosity, physical hardness and strength, and any discoloration or other evidence of incompatibility. Heat resistance was determined by autoignition tests in the case of the explosive samples and by 400°C furnace tests for unfilled binders.

Larger batches, 150-200 grams in size, were prepared with a Baker-Perkins model 2-PX one-pint mixer. Samples were mixed and cast under reduced pressure. Both preliminary and larger compositions were degassed and vibrated in the mold to compact and eliminate voids.

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APPENDIX B

TEST PROCEDURES

Reagent grade chemicals were used unless otherwise specified.

Autoignition Test

One-gram samples placed in an aluminum block with differential thermocouples leading to sample and reference wells were heated at 2°C/min. The ignition point was taken as the temperature of the reference thermocouple at time of ignition.

DTA was conducted with 30-50 mg samples heated at 3°C/min. Results by this method are generally about 20°C higher than by autoignition.

Oven tests were performed on inert binders with 0.5 - 1.0 gram samples placed in test tubes, covered to limit air circulation and put into a muffle furnace. Heating rates averaged 150°C per hour.

Sensitivity and Stability Tests

These are described in References 26 and 27.

Detonation Velocity

Cylindrical samples 0.5-inch diameter were detonated with a tetryl booster and velocity was measured by the pin switch method with oscilloscope records indicating firing times.

APPENDIX C

TABLE 11. Compositions Based on Vinyl-Addition Type Silicone Resins.
Resin binder plus DATB, TATB, or TACOT, approximately 50:50.

Binder components	Respective ratios	Viscosity of binder	Cured properties ^a	Autoignition point, °C			Binder in 350-400°C oven
				DATB	TATB	TACOT	
Sylgard 184/184 curing agent	10:1	Very poor, traps air	Binder firm but weak and granular. With filler, tough, dense, strong.	290	309	335	Excellent resistance, slight weakening. no exudation or charring.
184/184 curing agent/DC200/dicup	54:5:40:1.5	Fair, traps air	Binder "cheesy." With filler weaker & more flexible than above	307	328	315	Heavy fumes, 310-320. Slightly charred and very weak.
184/184 curing agent/ $\text{Vi}_2\text{Me}_4\text{Si}_2\text{O}/\text{dicup}$ ^b	78:7:21:0.5	Fair to good	Binder solid but soft and weak. With filler failed to cure
184/184 curing agent/ $\text{Vi}_2\text{Me}_2\text{Si}/\text{dicup}$	63:6:30:1.5 43:35:21:1.5	Fair to good	Failed to cure consistently. Better with more 184 curing agent but discolored & nonhomogeneous.	...	296	284
184/184 curing agent/ $\text{Vi}_2\text{Me}_2\text{Si}/\text{dicup}$	50:25:24:1.5	Milky, thixotropic	Soft, porous, discolored. Phenyl silane not compatible.
184/184 curing agent/styrene/dicup	63:6:30:1.5	Binder cured but milky and weak. With filler, porous and very weak.
184/184 curing agent/ $\text{Me}(\text{MeO})_3\text{Si}/\text{Pb octoate catalyst}$	69:7:24:0.2	Good	Varied with ambient humidity, solid & strong to soft, weak, and porous.	307	328	335	>360 crumbly and weak.
184/184 curing agent/ ViPS/dicup	45:33:21:1.5 57:14:28:1.5 50:25:24:1.5	Satisfactory Satisfactory Satisfactory	Binders firm but weak. With filler no satisfactory cures obtained.	...	315	327	Weak and crusted at 380.
GE RTV 615 A/B	10:1	Very poor	Tough, dense, strong	292	311	311 ^f	340 fumes, 355 weakened
615 A/B/DC 13308	60:6:34	Poor	Flexible, solid, fairly strong	309	333	360	Similar to above.
615 A/B/ ViPS/dicup	69:7:23:1.5	Satisfactory	Binder solid, resilient, slightly weak. Explosives tacky or porous.
Y 3467/3466/KL 1890	20:0.1:0.1	Very viscous	Rubbery, weak, granular	296-310	330	350
Y 3467/3466/KL 1800/ ViPS/dicup	54:44:0.2:0.2:1.5	Poor	Porous with explosives. Binder solid but weak. Explosives fairly strong & solid but discolored.	280	289	280
Y 3467/3466/KL 1800/ $\text{Vi}_2\text{Me}_2\text{Si}/\text{dicup}$	62:36:0.2:0.2:1.5	Poor	All compositions very porous.	308	322	334

^aCured at 80-125°C, 24-48 hours in cylindrical teflon molds.^bDivinyl tetramethyl disiloxane, Dow Corning.^cDivinyl dimethyl silane.^dDivinyl diphenyl silane.^eVinyl triisopropoxy silane.^fComparatively low results may be due to paraffin used to exclude air.^gDow Corning polydimethyl siloxane fluid.^hOther alkoxy and vinyl silanes and other curing agents were also tried. Results in the table are typical and representative of all.

APPENDIX D

TABLE 12. Alkoxy Silane Diluents in Eccosil Binder Compositions, Step Cured, Ambient to 125°C^a

Diluent(s)	Component ratio Eccosil/Silane/1330/Catalyst ^a respective pts/wt	Binder viscosity ^b	Cured properties		Autoignition point, °C
			Appearance	400°C oven test	TATB TACOT
Me(MeO) ₃ Si	10/7.2/0/0.004	Fair	Good strength and rigidity filled, erratic cure unfilled.	Not run. Unfilled binder did not cure adequately.	...
Me(MeO) ₃ Si/1330	5/5/0/0.002	Excellent	Porous. Very fast curing rate when filled.
	10/2/6/0.011	Fair	Flexible. Slightly weak and tacky.	Liquefaction on some samples >314°C.	365
Me ₂ (MeO) ₂ Si	10/4/4/0.004	Good	Weaker. TATB strongest.	Same as above.	...
Me ₂ (MeO) ₂ Si/1330	10/7/0/0.006	Good	Tough and rubbery, slightly porous.	330°C fumes, 380°C weaker, little visible change.	365
	10/2/6/0.019	Fair	Solid, slightly weak and stretchy. No cure without filler.	367
Et(EtO) ₃ Si	10/7/0/0.010	Good	No cure without filler. TATB incomplete cure, TACOT porous.	362
Et(EtO) ₃ Si/1330	10/2/6/0.024	Fair	Solid, strong, flexible, filled and unfilled.	Fumes 300-320; melts >320	366
Me ₂ (EtO) ₂ Si	10/7/0/0.008	Good	Very porous. Very fast cure.	Fumes 330-350. Little visible change >360. Slightly weaker.	365
Me ₂ (EtO) ₂ Si/1330	10/2/6/0.019	Good	Solid, rubbery. TATB best.	Fumes 320-340. Melts 350.	364
(EtO) ₄ Si/1330	10/0.5/8/0.012	Poor	Some porosity, fair strength, similar to Me ₂ (EtO) ₂ Si/1330.	367
φ(MeO) ₃ Si	10/7/0/0.003	Incompatible
φ(MeO) ₃ Si/1330	10/2/6/0.019	Fair	Incompatible on standing.
Me-φ(MeO) ₂ Si	10/7.1/0/0.008	Poor	Failed to cure.
Me-φ(MeO) ₂ Si/1330	10/2/6/0.009	Fair	Incomplete cure.	364
φ ₂ (MeO) ₂ Si/1330	10/2/6/0.019	Fair	Failed to cure.
φ(EtO) ₃ Si/1330	10/2/6/0.019	Fair	Binder, TATB, TACOT strong and resilient. DATB tacky.	367

^aEccosil 4712D.^bRelative and approximate only. All were inferior to EPX 147-2.

APPENDIX E

TABLE 13. Unsaturated Alkyl and Phenyl Silanes as Binder Components in Eccosil Formulations.
Cured ambient to 125°C without peroxide or paraffin unless indicated.

Silane additive	Binder ratio Eccosil/additive/catalyst ^a	Viscosity	Cured properties		Autoignition point, °C		
			Appearance	Oven test	DATB	TATB	TACOT
Allyl trimethyl	10:8:0.02 and 10:5:0.02	Fair	Hard, firm, strong, solid, resilient.	Little change.	308	334	362
Vinyl trimethyl	10:8:0.02	Satisfactory	Hard, firm, more rigid.	Softer & weaker, no severe decomposition.	308	334	364
Divinyl dimethyl	10:8:0.02 and 10:5:0.02	Satisfactory	Softer, weaker, more porous.	Binder incompletely cured.	305	335	355
Divinyl tetramethyl disiloxane	10:8:0.02	Higher than above, fair.	Firm, flexible, strong, solid.	Slight weakening & crusting.	308	332	358
Methyl trivinyl	10:5:0.02	Fair	Very porous but very strong.	323 ^b	319 ^b
Divinyl tetramethyl disiloxane/1330	10:2:6:0.032	Fair	Strong, flexible, tough.	330 fumes, 350 melts.	315	340	364
	Above + 1.5% dicup.	Fair	Solid, tough, slightly harder.	320 melts	311	331	349
	10:4:4:0.032	Good	Solid, flexible, slight rubbery.	350 loses shape. 380 exudation.	312	340	365
Divinyl diphenyl	Incompatible
Divinyl diphenyl/1330	10:2:6:0.032	Thixotropic	Tough, dense, fine grained.	330 melts, 350 completely liquid.

^aEccosil 4712D.

^bCured with paraffin.

TABLE 14. Unsaturated Alkoxysilanes as Diluents for Ecosil 4712 A-D Binder With Explosive Fillers.

Diluent system	Respective ratio 4712 - diluent parts by wt ^a	Viscosity	Cured properties		Autoignition, °C		
			Appearance	400 °C oven test	DATB	TATB	TACOT
Allyl triethoxy silane	10/8 & 10/5	Fair	Fairly hard, strong, & resilient binder alone variable.	Heavy fumes 338.	306	330	335
Diallyldiethoxy silane	10/8	Fair	Variable-rigid to elastic.	Weakening, slight discoloration.	305	325	337 ^b
With 1330 ^c	10/2/6 to 10/5/3	Poor to fair	Stronger & more solid with dicup.	10/5/3 no exudation, 10/2/6 melts at 330.	...	295	285 ^{b, d}
Triallylethoxy silane	10/5	Fair	Relatively hard but slightly weak, slightly porous.	Brown fumes & slight weakening.	298	320	332 ^d
Mixed allylethoxy silane ^e	5/5	Fair to good	Hard, fair strength, relatively rigid and solid.	Heavy fumes 330.	305	330	349
Vinyl triethoxy silane	10/8 & 10/5	Fair	More rigid with increased (OEI). Fair strength.	White crust, little change.	305	322	320
Vinyl methyl diethoxy silane	10/8	Fair	Porous, relatively soft and flexible.	308	330	338
Vinyl dimethyl ethoxy silane	10/8 & 10/5	Fair to good	Porous but tough and resilient.	309	336	360
With 1330 ^c	10/4/4	Fair	DATB porous, TATB & TACOT solid, flexible, strong.
Vinyl triisopropoxy silane	10/8	Fair	Solid, hard, strong, resilient.	Some weakening & discoloration.	306	329	343
With 1330 ^c	10/1/7 to 10/6/2	Fair	Rigidity varies with % VIPS. All solid and strong.	Crusting & fumes at 320 with low 1330. Liquefaction at 360 with 7 parts 1330.	285-305	317-325	317-318 ^{b, d}
Methacryloxy propyl trimethoxy silane (Z 6030)	10/8	Mediocre	Variable, some porosity.	Charred and brittle.	284	298	280
Tetra alloxysilane	10/7	Good	Porous, weak, poor cure.
With 1330 ^c	10/1/7 & 10/.5/8	Fair	Very reactive, gelled in mixing.
Vinyl triacetoxysilane	10/5	Immiscible

^a 4712D = 0.2% 4712A. Most were cured both without and with 1-1.5% dicup.^b 1 - 1.5% dicup in formulation.^c 1330 last value in ratio.^d Cured with paraffin.^e Commercial blend.

TABLE 15. Unsaturated Hydrocarbon Monomers Used as Diluents for Eccosil 4712A.
Cured ambient to 125°C.

Diluent	Component ratio Eccosil ^a /diluent	Viscosity	Cured properties		Remarks
			Appearance	Autoignition, °C TACOT	
Styrene Styrene/1330 Diallylphthalate	10/7.2 10/12/6	Good Fair Immiscible	Solid & tough but porous Tough, rubbery, a few voids.	266 ^{b, c} 291 ^{b, c}	Cured with & without dicup. Liquefaction ~ 350°C
Divinylbenzene Butyl acrylate Decyl acrylate	23/13.7 10/5 3/4	Good Good Fair	Tough, rubbery, a few voids. Tough but porous. Weak and porous	293 ^{b, c} 299 ^{b, c}	Cured with 1.5% dicup. Cured with dicup & paraffin.
Methyl methacrylate Ethylene dimethacrylate C ₇ & C ₅ fluoroacrylates	5/4	Good Immiscible Immiscible	Tough but porous
Acrylonitrile	10/5	Thixotropic	Hard, firm, rubbery	333 ^b	Cured with paraffin with and without dicup.
Vinyl pyrrolidone Diallyl Sebacate	10/5 10/5/0.02	Immiscible Questionable miscibility
Butenediol/1330 Trimethylol propane diallyl ether	10/5/5/0.05 10/5/0.02	Immiscible Binder tough, elastic, greasy texture. TACOT filled-spongy. Exotherm 255 ^b Cured with and without dicup. Latter discolored.

^a 4712D = 0.2% 4712A.

^b Cured with paraffin.

^c Contains dicup. -

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DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Naval Weapons Center China Lake, California 93555		2a. REPORT SECURITY CLASSIFICATION CONFIDENTIAL
		2b. GROUP 4
3. REPORT TITLE CASTABLE HEAT RESISTANT EXPLOSIVE COMPOSITIONS CAPABLE OF WITHSTANDING 500°F AND HIGHER (U)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Progress Report		
5. AUTHOR(S) (Last name, first name, initial) STOTT, Barbara A.		
6. REPORT DATE December 1967	7a. TOTAL NO. OF PAGES 60	7b. NO. OF REFS 27
8a. CONTRACT OR GRANT NO. b. PROJECT NO. RUME TA-3E-015/216-1/F008-10-004 (Prob. 15) 1964 c. RMMO-62-063/216-1/F009-08-05 1965 ORD-033-201/200-1/F009-08-05 1966 d. ORD-033-201/200-1/F009-08-05/MIPR PG 7-6.		9a. ORIGINATOR'S REPORT NUMBER(S) NWC TP 4461 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
10. AVAILABILITY/LIMITATION NOTICES IN ADDITION TO SECURITY REQUIREMENTS WHICH APPLY TO THIS DOCUMENT AND MUST BE MET, EACH TRANSMITTAL OUTSIDE THE DEPARTMENT OF DEFENSE MUST HAVE PRIOR APPROVAL OF THE NAVAL WEAPONS CENTER.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Naval Ordnance Systems Command Naval Material Command Washington, D. C. 20360
13. ABSTRACT In an attempt to develop a castable explosive resistant to temperatures of 500°F or higher, TACOT, TATB, DATB, and in a few cases, TNC were combined with a variety of binder types. These included epoxies, polyesters, vinyls, plastisols, silicone rubbers and various combinations. The silicones were the most promising in respect to heat resistance. However, their high viscosity required the use of diluents which introduced curing difficulties, and their unfavorable decomposition thermodynamics affected detonation characteristics adversely. Epoxies and polyesters at relatively low temperatures exhibited exotherms which were in some cases sufficient to ignite the explosive fillers well below their autoignition points. Plastisols and vinyls were less heat stable than silicones, with stability in the case of unsaturated compounds reduced still further by inclusion of peroxide curatives and paraffin used to exclude air in curing. Explosive fillers, in particular TATB, were difficult to incorporate to high solids loadings because of their fine particle size. Insolubility of both TATB and TACOT in common recrystallizing solvents made size modification difficult or impossible. TACOT was superior in respect to autoignition characteristics, with decomposition in the neighborhood of 350°C. Ruby calculations to predict detonation properties indicate that with improved solids loadings and inclusion of an additive such as potassium perchlorate, TACOT compositions may show a detonation velocity greater than 6000 meters per second and detonation pressures on the order of 150 K-bars. These values may depend on optimization of binder structure as well as experimental verification of constants and assumptions used in performing computations. (CONFIDENTIAL)		

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